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Charles R. Langer

INTRODUCTION

TO

CHEMICAL ANALYSIS

FOR BEGINNERS

From the Sixth German Edition

...OF...

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The thanks of the Translators are due to Prof. Rüdorff for permission to translate and to adapt with such additions as seemed proper, and to Prof. Jas. H. Shepard for the use of the table, "The Natural Classification of the Elements," with explanatory notes.

INTRODUCTION.

It is generally conceded that chemistry cannot be properly learned by the student except through the medium of individual experimental work in the laboratory. Lectures and recitations serve to present the fundamental laws of general chemistry and chemical philosophy and furnish a splendid field for experiments on an elaborate scale to illustrate these laws; but only work in the laboratory will familiarize the student with chemical changes and the properties of the elements and their compounds.

Beginners usually reason from the specific to the general, hence a clear understanding of the specific properties of a limited number of chemical elements and their compounds will lay a better foundation for an accurate and broad knowledge of the science than a more extended but less systematic course of study.

This little book originally designed for Prof. Rüdorff's pupils has met with such marked favor in Germany, having passed rapidly through six large editions, that the translators have been induced to offer it for the consideration of the American teacher and pupil, believing it fully fills the requirements, as herein set forth. As a guide to the student in the introductory study of the chemistry of the elements and their compounds, the popularity this work has attained at home is proof enough of its excellence.

The special feature of the book is the originality the author displays in presenting to the student chemical changes in a manner at once tangible and interesting. Pro-

fessor Rüdorff's method of teaching is best explained in his introductory remarks, as follows:

"Work in the chemical laboratory has a marked attraction for the majority of students at first. The original warm ardor, however, will often be observed to cool off in consequence of the many failures incurred. Experimenting in private, without the aid of a competent teacher or guide, and students' work in the laboratory is too liable to degenerate into unsystematic testing and play with chemicals, which results only in the most discouraging failure to attain the desired object.

"The careful pursuit of elementary analytical chemistry will train the student to exact observation and correct interpretation of the same, and will give him an excellent scientific training besides developing manipulative skill. In order that this aim may not fail, the laboratory work must be based on a systematic and thorough plan. There must be a gradual succession from easy to more difficult tasks. Particular stress should be laid on this point; that the student be made to understand fully the reasons for an operation, and why it is pursued in a particular manner and not otherwise, In order to accomplish this, he must be well acquainted with the reactions of the various chemicals and have an insight into the nature of the chemical changes which take place under his observation.

"It is a well-known fact, that the beginner in analytical chemistry is often disheartened by the extent of the field to be covered, therefore, first of all, the subjects to be treated of in an elementary work should be selected within quite narrow limits.

"The author has endeavored to set forth the principles of analytical chemistry with a limited number of elements and their more important compounds. In selecting such

substances due consideration has been given to the fact of the limited facilities of most laboratories.

"The book is divided into two parts: in Part I. the reactions of the most important elements are studied, particular salts, or compounds being employed. The characteristic tests are marked with a *. The student examines the majority of the substances numbered and makes himself familiar with them (with the aid of the teacher, if necessary), and with the manipulations of reactions as well as with the nature of the chemical changes which take place. The equations are to be written out on the blank pages.

"This introductory work done, the student proceeds to Part II., which treats of the examination of given substances. This part consists of two subdivisions or chapters. The first is of a preparatory character, being confined to simple substances containing not more than one base and one acid. The metals, or bases, are Am, Na, K, Ba, Sr, Ca, Mg, Al, Cr, Fe, Mn, Co, Ni, Zn, Cd, Pb, Bi, Cu, Ag, Hg, Sb, As, Sn, and they may be present as oxides, sulphides, sulphates, chromates, phosphates, borates, nitrates, carbonates, arsenites, or antimonides. When the constituents are found, confirmatory tests should be made from memory or by the aid of Part I.

"After a sufficient number of analyses have been made and the remainder of Part I. has been taken up, the student, thus advanced, proceeds to the second section of Part II. which extends the limited scheme of the first section to the analysis of complex substances or mixtures of the salts containing more than one base or one acid. This plan is a little more limited, however, than the first, as regards the number of constituents allowed. Chromium and strontium are entirely excluded in complex substances, and the metals arsenic, antimony and tin, are allowed only on condition

that not more than one of them shall be present at the same time. This will also apply to the metals nickel and cobalt; neither is there allowed more than one constituent at a time which is insoluble in both water and acids. The peculiar difficulties connected with the separation and determination of the substances named will, it is hoped, be sufficient excuse for these limitations, if the aim of the book and the limited facilities, often at the command of the student, are kept in view."

In preparing the work of Prof. Rüdorff we have made a few additions calculated to assist the medical and dental student who suffers mainly the disadvantage of being unable to devote but a small part of his time to chemical studies, and who, in consequence, is not quite so well posted on many points as might be desired. As a matter of fact, the medical and dental student has an undue amount of trouble and sustains a consequent loss of time from this very source, and is liable to become disheartened and disgusted with chemistry in general. For his benefit, and in order to be a little more explicit, we have inserted a few short explanatory remarks. The principal additions have been in giving the chemical formulas of the substances worked with and of the precipitates or new substances formed, with the exception, however, of those of indefinite compounds, such as basic salts.

We have given, in addition, the common, the chemical and the Latin names of the U. S. Pharmacopœia, when ever practical, to all substances met with, which are of technical or medicinal value, believing that all students are familiar with most substances under at least one of these titles.

THE TRANSLATORS.

LABORATORY OUTFIT.

APPARATUS.

1. Test tube rack with one doz. test tubes.
2. Two small funnels.
3. Filter paper.
4. A pair of shears.
5. Wash bottle.
6. Iron ring stand, with sand bath or wire gauze.
7. Small hard-glass tubes with closed ends, two and a half or three inches long.
8. One or two small evaporating dishes.
9. Spirit lamp or Bunsen burner; adapted for a luminous flame for blow pipe experiments.
10. Blowpipe.
11. A piece of charcoal.
12. A pair of tongs or pincers.
13. Platinum foil and wire.
14. Two glass rods.

REAGENTS.

A. LIQUIDS AND SOLUTIONS.

H_2SO_4 conc.	Sulphuric Acid conc.	Spec. grav. = 1.84.
H_2SO_4 dil.	Sulphuric Acid dil.	5 vol. acid : 100 water.
HCl dil.	Hydrochloric Acid.	C. P. sp. g. = 1.12.
HNO_3 dil.	Nitric Acid.	C. P. sp. g. = 1.20.
H_2S	Hydric Sulphide.	Freshly prepared saturated sol.
$(NH_4)_2S$	Ammonic Sulphide.	Yellow, 1 : 1, + ½ vol. dilute NH_4OH.
NH_4OH	Ammonic Hydrate.	1 vol. U. S. P. Aqua Am. : 1 vol. water.
NaOH	Sodic Hydrate.	Sp. g. = 1.12.
$(NH_4)_2CO_3$	Ammonic Carbonate.	20 : 100 + ¼ Am. Hydrate.
Na_2CO_3	Sodic Carbonate.	20 : 100.
Na_2HPO_4	Sodic Hydric Phosphate.	10 : 100.
$MgSO_4$	Magnesic Sulphate.	10 : 100 + 5 NH_4Cl.
NH_4Cl	Ammonic Chloride.	30 : 100.
$BaCl_2$	Baric Chloride.	5 : 100.
$AgNO_3$	Argentic Nitrate.	5 : 100.
$K_4(FeCy_6)$	Potassic Ferrocyanide.	5 : 100.

$K_6(Fe_2Cy_{12})$	Potassic Ferricyanide.	5 : 100.
$K_2Cr_2O_7$	Potassic Dichromate.	10 : 100.
KI	Potassic Iodide.	5 : 100.
$Pb(C_2H_3O_2)_2$	Plumbic Acetate.	5 : 100.
$CaSO_4$	Calcic Sulphate.	Saturated Solution.
	Ammonic Molybdate.	6 : 100 + 1 HNO_3.
	Sol. Indigo.	1 : 6 H_2SO+SO_3 (Nordhausen).
$H_2C_4H_4O_6$	Tartaric Acid.	25 : 100.
$H_2C_2O_4$	Oxalic Acid	Saturated (12 : 100).
$(NH_4)_2C_2O_4$	Ammonic Oxalate.	8 : 100.
KCyS	Potassic Sulphocyanide.	5 : 100.
$CuSO_4$	Cupric Sulphate.	5 : 100.
$HgCl_2$	Mercuric Chloride.	5 : 100.
	Fuming Nitric Acid.	
	Tincture of Galls.	1 : 1 Alcohol, 4 Aq.
C_2H_5OH	Alcohol	U. S. P.

B. DRY REAGENTS AND CHEMICALS FOR EXAMINATION.
USED BY ALL STUDENTS IN COMMON.

1. Litmus paper, blue and red.
2. Anhydrous sodic carbonate.
3. Nitre (pulverized).
4. Borax (pulv.).
5. Cupric sulphate.
6. Ferrous sulphate.
7. Manganous sulph.
8. Magnesic sulph.
9. Cadmic sulph.
10. Nickel sulph.
11. Cobalt sulph.
12. Alum.
13. Baric Chloride.
14. Ammonic chloride.
15. Sodic phosphate.
16. Plumbic nitrate.
17. Potassic dichromate.
18. Potassic iodide.
19. Starch.
20. Marble.
21. Strontic carbonate.
22. Minium.
23. Black oxide of manganese.
24. Arsenious anhydride and met. arsenic.
25. Copper turnings.
26. Tin, granulated.
27. Scrap zinc or granules.
28. Iron wire or tacks.
29. Bismuth.
30. Antimony.
31. Heavy spar (pulv.).
32. Iron pyrites (pulv.).

Certain pieces of apparatus and the majority of reagents may be employed by several students in common.

QUANTIVALENCE OF METALS.

Monovalent.	Divalent.	Trivalent.	Tetravalent.
K	Ba Sr	Bi	Sn (stannic)
Na	Ca Mg	Sb (antimonous)	Pt (platinic)
Am	Mn Zn	As (arsenious)	
Ag	Fe (ferrous)	Au	
Hg (in mercurous compounds).	Co Ni		Hexavalent Double-atoms.
	Cd Pb		Fe_2
	Cu		Al_2
	Hg (mercuric)		Cr_2
	Sn (stannous)		
	Pt (platinous)		

BASICITY OF ACIDS.

Monobasic.	Dibasic.	Tribasic.	Tetrabasic.
HCl	H_2SO_4	H_3PO_4	$H_4(FeCy_6)$
HI	H_2CrO_4	H_3AsO_3	Hexabasic.
HNO_3	H_2CO_3	H_3AsO_4	$H_6(Fe_2Cy_{12})$

The student should remember that neglect of precautions and haste will spoil his experiments. Always keep in mind the following rules:

1. Read ahead until you understand the point and then follow out directions carefully.

2. Be on your guard especially against employing excess of reagents or of heat. Excesses may spoil everything; insoluble substances may become soluble and *vice versa*. For instance:

Dil. HCl dissolves $BaCO_3$, but conc. HCl will not.

Dil. HCl does not dissolve PbS, but hot conc. HCl will.

$PbCl_2$ is soluble in water in presence of but little HCl, but is precipitated by addition of conc. HCl.

Most all reactions being based on the phenomena of solubility and insolubility, the importance of the above rules is apparent.

TABLE OF SOLUBILITIES.

	K	Na	NH_4	Ba	Sr	Ca	Mg	Al	Mn	Fe	Fe_2	Co
Oxide	1	1	1	1	1	1-2	2	2	2	2	2	2
Sulphide	1	1	1	1	1	1-2	2	..	2	2	..	2
Chloride	1	1	1	1	1	1	1	1	1	1	1	1
Iodide	1	1	1	1	1	1	1	1	1	1	..	1
Sulphate	1	1	1	3	3	1-3	1	1	1	1	1	1
Nitrate	1	1	1	1	1	1	1	1	1	1	1	1
Carbonate	1	1	1	2	2	2	2	..	2	2	..	2
Phosphate	1	1	1	2	2	2	2	2	2	2	2	2
Arsenite	1	1	1	2	2	2	2	..	..	2	2	2
Chromate	1	1	1	2	1-2	1-2	1	2	1	..	1	2
Borate	1	1	1	2	2	2	2	2	2	2	2	2
Oxalate	1	1	1	2	2	2	2	2	2	1-2	1-2	2

	Ni	Zn	Cd	Pb	Cu	Bi	Hg	Ag	Cr_2	Sn	As	Sb
Oxide	2	2	2	2	2	2	2	2	2 & 3	2 & 3	1-2	2
Sulphide	2	2	2	2	2	2	3	2	..	2	2	2
Chloride	1	1	1	1-3	1	2	1 & 3	3	1 & 3	1	1	2
Iodide	1	1	1	1-3	..	..	2	3	..	1	1	..
Sulphate	1	1	1	3	1	2	2	1	1	..	..	2
Nitrate	1	1	1	1	1	2	1	1	1	..	..	..
Carbonate	2	2	2	2	2	2	2	2	..	..	..	..
Phosphate	2	2	2	2	2	2	2	2	2	2	2	..
Arsenite	2	2	2	2	2	2	2	2	..	..	..	..
Chromate	2	2	2	2-3	2	2	2	2	..	..	..	2
Borate	2	2	2	2	2	2	2	2	2	2	2	..
Oxalate	2	2	2	2	2	2	2	2	1	2	2	..

The preceding table gives the solubility, in water and acids, of the most important metallic oxides, sulphides, chlorides, iodides and other salts. The meaning of abbreviations is:

1, Soluble in water.
2, Insoluble in water, soluble in hydrochloric or nitric acid.
3, Insoluble in both water and acids.
1–2, Soluble in water with difficulty, but readily in acids.
1–3, Soluble with difficulty in both water and acids.
2–3, Insoluble in water, soluble with difficulty in acids.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
R_2O	RO	R_2O_3	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	
H 1							
Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5	
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe, Ni, Co 56 58.6 59
Cu 63	Zn 65	Ga 69	— 72(?)	As 75	Se 79	Br 80	
Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100(?)	Rh, Ru, Pd 104 104.5 106
Ag 108	Cd 112	In 114	Sn 118	Sb 120	Te 128	I 127	
Cs 183	Ba 137	La 139	Ce 141	Di 144	— 149(?)	— 150(?)	— — —
—	—	—	—	Er 166	— 167(?)	— 169(?)	
— 170(?)	— 172(?)	Yb 173	— 178(?)	Ta 182	W 184	— 190(?)	Ir, Os, Pt 192.5 193 194
Au 176	Hg 200	Ti 204	Pb 207	Bi 209	—	—	
—	—	—	Th 232(?)	— 237(?)	U 240		

In this table the elements are arranged in eight vertical columns, representing eight groups; while successive series are presented in nearly horizontal lines. These are made to incline slightly, so that on rolling the table Na will immediately succeed F; K will succeed Cl, and so on in a spiral line. The first eight or twelve elements present very marked individuality of character; some of these are typical of natural groups which follow. Elements of most distinct basic character are found towards the left; non-metals predominate in the upper and middle parts of Groups V., VI., and VII.; while the lower part of the table is marked by the more indifferent elements. A double spiral will be traced beyond Si (beginning with P and V respectively) and distinguished by **heavy-face** and light-face type.

Many familiar relationships can now be traced out; thus, K, Rb, and Cs are more closely related to each other than they are to Li and Na; Ca, Sr, and Ba are very closely related in their properties, while Mg resembles these elements in some respects and Zn and Cd in others. Very many facts in regard to the properties and compounds of the several elements may be fixed in the mind by the law of association when studied with the aid of this table, while they could only be retained by a severe effort of memory, if viewed independently.

It will be noticed that the first series has but one member; group VIII. is represented in the even series only, beginning with the fourth; and the element of highest atomic weight yet discovered is in the twelfth series, group VI. It is necessary to transpose I and Te in the table, in view of their properties. The blanks represent the probable position and approximate atomic weights of elements not yet discovered or investigated. When Mendelejeff published his table (in 1869) he left two blanks which have since been filled by Sc and Ga; and the properties of these elements agree very closely with those expressly predicted from the analogies indicated in the table. The true position of some of the rarer metals (especially those of the cerium group) is still uncertain; these are here arranged as in Muir's *Principles of Chemistry*.

The harmony of nature here exhibited is most impressive. Is it possible that the so-called elements are really compounds? Did the various "elements" of the earth and sun once exist as hydrogen, when our solar system was a nebula?[1] And will modern chemists ever revive the famed problem of the alchemists, and seek to turn the base metals into gold? Far more precious than gold is the search for *truth;* and the more we learn of science, the broader becomes our conception of what we know in part, and the deeper should be our reverence for the infinite thought of the Creator.

[1] See a paper by F. W. Clark in *Popular Science Monthly* for Feb. 1876, p. 463.

From SHEPARD'S CHEMISTRY.

TO THE STUDENT.

1. Each pupil is held responsible for the condition of his desk and apparatus, and is required to leave everything clean and in good order.
2. Pupils are held responsible for breakage and the careless and wasteful use of chemicals and gas.
3. Pupils are cautioned not to mix chemicals nor to make experiments other than those given in the instructions.
4. In using reagent bottles, never lay the stoppers down; hold them between the fingers and replace at once.
5. In applying reagents add drop by drop unless otherwise instructed.
6. Nothing should be put into reagent bottles, not even stirring rods or test paper. Never pour back a reagent once removed from its bottle.
7. Strong acids, solid matter, solutions of mercury, silver or platinum, must not be thrown into the sinks. Jars are supplied for these purposes.
8. Silver, platinum and gold slops must be saved in jars used for that purpose.
9. CAUTION. Glass and porcelain ware must be clean and dry on the outside before being heated, and must be heated carefully to avoid breakage.
10. Acids must be evaporated in the fume chambers. In evaporating solutions to dryness in glass or porcelain dishes use the water bath to avoid breakage.
11. Make your own experiments, use your own hands, eyes, reasoning faculties and common sense, and let your neighbor do the same.
12. Make your notes carefully and clear, using symbols and formulæ and equations when possible.
13. Each student should have towels and clean cloths for wiping and cleaning apparatus.
14. Follow rules carefully on page xiii. in relation to reactions.

PART I.

REACTIONS.

I. COPPER.

Boil some copper turnings with some hydrochloric or sulphuric acid (dil.); they remain unchanged.

Heat a few other turnings with nitric acid. The metal dissolves rapidly to blue *cupric nitrate*, $Cu(NO_3)_2$, with the formation of copious reddish-brown fumes of NO_2 (the result of the reduction of HNO_3, NO being oxidized by the air into NO_2).

Cupric Sulphate = $CuSO_4 + 5aq$.

(Blue Vitriol, Cupri Sulphas U. S. P.)

Dissolve a piece of the salt the size of a bean in a test tube one-third full of water by heating, and take about one-tenth of this solution for each reaction; for reactions under headings 3-9 dilute each portion with 5-6 volumes of water before adding the reagent. The blue solution has an acid reaction, *i. e.*, turns blue litmus paper red. Reagents act upon it as follows:

Reactions for the Base.

1. **Zinc (or Iron)** immersed in the solution, precipitates *metallic copper* on the zinc (or iron). In the liquid, cupric sulphate is replaced by zinc sulphate.

*2. **Hydric Sulphide** solution (6-8 volumes to the copper solution), *brownish-black copper sulphide*, CuS. Heat the test tube gently and the precipitate will more rapidly collect and settle to the bottom upon standing. Pour off the supernatant liquid

*Characteristic test.

cautiously and as completely as possible, and divide the remaining liquid with the precipitate in it into two portions. To one portion add a few drops (4-5) of *nitric acid*, to the other a few drops of *hydrochloric acid*, and heat both to boiling. The precipitate remains unchanged by HCl, but dissolves in HNO_3, with the separation of a *dirty-gray sulphur* which floats on the surface of the liquid.

3. **Ammonic Sulphide** (4-5 drops) forms the same precipitate, CuS; an excess of the reagent (say 10 drops) will not dissolve the precipitate, even upon heating.

4. **Sodic or Potassic Hydrate** (10-20 drops), *blue copper hydroxide*, $Cu(OH)_2$, which on boiling is converted into *dark brown copper oxide*, CuO.

*5. **Ammonic Hydrate** (2-3 drops), *bluish-green basic sulphate* (*i. e.*, a combination of the neutral salt with its own hydroxide); it dissolves on the addition of more NH_4OH with *blue color*. To one drop of the original copper solution in a test tube full of water add a drop of NH_4OH; it produces a decided blue color.

6. **Ammonic Carbonate,** *bluish-green basic copper carbonate*, which is soluble in an excess of the reagent.

7. **Sodic Carbonate,** *bluish-green basic copper carbonate.*

*8. **Potassic Ferrocyanide** (a few drops), *reddish-brown* Cu_2Cfy ($=Cu_2FeCy_6$). Dilute one drop of the copper solution with a test tube full of water, and add thereto a few drops of potassic ferrocyanide. The liquid will become distinctly brown on shaking.

Reactions for the Acid.

*9. **Baric Chloride** (a few drops) white *baric sulphate*, $BaSO_4$, which is insoluble upon addition of acids (HNO_3 or HCl).

10. Heat a small piece of blue vitriol in a glass tube closed at the lower end. It turns light gray by giving off its water of crystallization, which condenses farther up on the sides of the tube.

Blowpipe Reactions.

11. Dip the red-hot looped end of the platinum wire into powdered borax and heat what sticks to the wire in the flame of a Bunsen burner. The borax bubbles and swells up, and finally melts to a clear bead (borax bead, borax glass). Melt together with this bead a piece of blue vitriol the size of a pin head by the aid of the blowpipe. On cooling, the bead will show a *green color* from copper.

12. Mix a small crystal of blue vitriol with 4-8 parts of anhydrous sodic carbonate and melt the mixture thoroughly on a piece of charcoal before the blowpipe. A great deal of carbonic acid (CO_2) escapes during the process, the charcoal (a powerful reducing agent when hot) having combined with the oxygen of the soda and of the copper-salt, leaving the sulphur of the latter to combine with the sodium of the former producing Na_2S (Hepar). Place some of this fused mass on a *bright* silver coin and moisten with a drop of water; a *brown spot* of Ag_2S will be formed on the coin after standing. Whenever silver tarnishes, this is due to the presence of at least a trace of hydric or some other soluble or volatile sulphide. The copper of the blue vitriol is contained in above-named hepar as minute scales. A few larger ones may be detected with the naked eye by grinding some of the hepar with water in a mortar.

13. Heat a small piece of a copper turning before the blowpipe on charcoal. It will fuse and be burned to *black oxide*, CuO.

II. ZINC.

Pour some hydrochloric acid on a few small pieces of zinc in a test tube and *warm moderately* until the liberation of gas has ceased. The metal dissolves with the evolution of hydrogen gas and the formation of:

Zinc Chloride=$ZnCl_2$

(Zinci Chloridum U. S. P.)

In order to get a solution which contains no free acid, it is necessary that there remain some undissolved zinc when the evolution of gas is over, in this solution, diluted with 6 volumes of water, reagents will produce the following changes:

Reactions for the Base.

1. **Hydric Sulphide** (6-8 vols. of the zinc solution), voluminous *white zinc sulphide*, ZnS. The precipitate dissolves readily on addition of several drops of HCl (chemical solution, resulting in the restoration of the original compound). Add to another portion of the zinc solution a few drops of HCl and then H_2S; no precipitate.

*2. **Ammonic Sulphide** (4-6 drops to the highly diluted sol.), white zinc sulphide, ZnS. To one portion of this precipitate add HCl; precipitate dissolves, but a slight turbidity remains which is due to the separation of some sulphur. Add sodic hydrate to another portion of the precipitate; it is not dissolved.

*3. **Sodic or Potassic Hydrate** (a few drops), *white zinc hydroxide*, $Zn(OH)_2$ which is redissolved on the addition of more of the precipitant. From this solution H_2S throws down ZnS (comp. **XIII.**, 3).

4. **Ammonic Hydrate** (at first only a few drops, then more), the same as in 3. If previously the same vol. of ammonic chloride sol. has been added to the zinc solution, NH_4OH will not produce a precipitate. This is due to the formation of ammonium, zinc double chloride, which is unaffected by the precipitant. For this reason, the NH_4OH precipitate cannot be obtained if the zinc solution contains much free acid.

5. **Sodic Carbonate,** *white basic zinc carbonate*, $ZnCO_3 + 2Zn(OH)_2$ (zinc carbonate, minus some of its carbonic acid, plus water=basic carbonate). Convince yourself of the liberation of CO_2 by repeating the experiment with hot zinc solution when the CO_2 will not remain absorbed in the liquid.

Reactions for the Acid. *6. **Argentic Nitrate,** white *silver chloride,* AgCl, which on shaking collects in a curdy mass. To some of the precipitate add a few drops of ammonic hydrate, to the balance a few drops of nitric acid; it will rapidly dissolve in the former, but not in the latter.

Blowpipe Reactions. 7. Fuse a small piece of zinc on charcoal before the blowpipe. The zinc burns with the formation of white fumes, which are partly deposited on the coal. This "coating" is yellow while hot and white when cold (=ZnO; Zinci Oxidum U. S. P.)

8. *Fuse some zinc salt with about 6 parts of dry sodic carbonate on charcoal before the blowpipe; zinc is reduced from the compound (comp. **I.,** 13), but no faster than it burns off, forming a coating of ZnO beyond the flame. For this reason no globule of metal can be found in the fused mass.

III. MANGANOUS SULPHATE=$MnSO_4$+7aq.

Dissolve as much of the salt as the point of a knife will hold in a test tube full of water by the aid of heat. The solution has an acid reaction. From the solution, diluted with more water, there will be precipitated by:

Reactions for the Base. 1. **Hydric Sulphide** nothing.

*2. **Ammonic Sulphide** (a few drops) flesh *colored manganous sulphide,* MnS, which turns dark brown by oxydation upon a short exposure to the air.

*3. **Sodic or Potassic Hydrate,** white *manganous hydrate,* $Mn(OH)_2$, which, in contact with the air, turns brown.

4. **Ammonic Hydrate** produces the same precipitate.

5. **Sodic Carbonate,** white *manganous carbonate,* $MnCO_3$.

Reactions for the Acid. *6. **Baric Chloride,** white *baric sulphate,* $BaSO_4$, insoluble in HCl, a few drops (comp. **I.,** 9.)

Blowpipe Reactions. 7. If a little of the salt is fused with 6 parts of dry sodic carbonate on charcoal before the blowpipe, the fused mass will blacken a moist silver coin.

8. *Ignite an exceedingly small piece of the salt on platinum foil over a Bunsen burner, with a mixture of 2 parts of sod. carb. and 1 part of nitre. It gives a *dark green fusion* of *potassic manganate*, K_2MnO_4. If too much of the manganese compound has been taken the color of the fusion will be so intense as to appear black.

9. *The borax bead will be colored *violet* by a very small piece of the salt.

IV. IRON.

Warm several small tacks or pieces of iron wire with HCl in a test tube until the evolution of gas has completely ceased; pour off the solution from the undissolved iron and divide it into 2 parts. The solution contains:

Ferrous Chloride = $FeCl_2$.

Dilute one part of the solution with 10 volumes of water. In this solution reagents will produce the following changes:-

Reactions for the Base. 1. **Hydric Sulphide** no change.

*2. **Ammonic Sulphide** (3-5 drops), *black ferrous sulphide*, FeS. Add several drops of HCl to some of the precipitate; it dissolves; but a slight, permanent turbidity remains, due to the separation of sulphur.

3. **Sodic or Potassic Hydrate,** *greenish ferrous hydrate*, $Fe(HO)_2$, which, in the upper part of the tube, where it comes into contact with the air, will become a dirty green and finally brown, owing to the formation of ferric hydrate.

4. **Sodic Carbonate** precipitates *white ferrous carbonate*,

$FeCO_3$ which, in contact with the air, turns dirty green and finally brown (formation of ferric hydrate).

5. **Potassic Ferrocyanide** (a few drops), a *light blue precipitate* which turns darker by contact with the air.

*6. **Potassic Ferricyanide,** a *dark blue precipitate* of $Fe_3(Cfy)_2(=Fe_3Fe_2Cy_{12})$ Turnbull's blue.

To the other part of the ferrous chloride solution add 8-10 drops of nitric acid and 2-3 drops of hydrochloric acid, and boil. The former serves to oxydize the H of the latter to H_2O and set free Cl. The ferrous is converted into reddish-brown ferric chloride. The intermediate black color of the liquid is due to the absorption of nitrogen oxide, NO (reduced from HNO_3, see **I.**) in an, as yet, unoxidized portion of the ferrous solution. Boil, if necessary with addition of a few drops of HNO_3, until a drop of the fluid diluted with some water will yield a reddish-brown precipitate with sodic hydrate. Be careful not to use more HNO_3 than is absolutely necessary. If this should have been the case, however, neutralize the excess of acid by adding NH_4OH drop by drop; but not so much as to produce a precipitate that will not redissolve upon shaking. Reagents will produce the following reactions in this solution of

Ferric Chloride$=Fe_2Cl_6$.

(Ferri Chloridum U. S. P.)

Reactions for the Base.

*7. **Hydric Sulphide,** slightly yellow or white sulphur with the reduction of the ferric or ferrous solution.

8. **Ammonic Sulphide** (4-6 drops) *reduces* the *ferric* to *ferrous* solution, and then precipitates *black ferrous sulphide,* FeS. If the solution is extremely dilute, NH_4HS will only color it a dark green. If there is much free acid in the solution, the FeS precipitate will disappear on shaking and more NH_4HS must be added.

*9 **Sodic or Potassic Hydrate,** *yellowish-brown ferric hydrate,* $Fe_2(OH)_6$ (Ferri Peroxidum Hydratum U. S. P.), which is insoluble in an excess of the precipitant.

10. **Sodic or Ammonic Carbonate,** *yellowish-brown,* $Fe_2(OH)_6$; CO_2 escapes.

*11. **Potassic Ferrocyanide** (a few drops) precipitates *Prussian blue,* Fe_4Cfy_3 [$=Fe_4(FeCy_6)_3$]. Even very dilute solutions will be colored a distinct blue by this reagent. Liquids to be tested with Ky_4Cfy must be but slightly acid; else errors will occur.

12. **Potassic Ferricyanide** only colors the solution dark or brown without producing a precipitate (comp. ferrous reaction).

*13. **Potassic Sulphocyanide** colors the solution *blood-red* (*extremely delicate test*). The solution must contain some free acid.

14. **Tannic Acid or Tincture Galls** throws down *black ferric tannate* (ink).

Blowpipe Reactions. 15. Before the blowpipe, iron burns to *ferro ferric* or *magnetic oxide,* Fe_3O_4 (blacksmith's scale). This or a small piece of copperas (ferrous sulphate) colors the borax bead in the reducing flame *greenish,* in the oxydizing flame *yellow* to brown, which, on cooling, gradually becomes lighter colored.

V. LEAD.

Lead is scarcely affected by hydrochloric or sulphuric acids, but dissolves in warm nitric acid with the liberation of red fumes (comp. **I.**) and the formation of

Lead Nitrate $= Pb(NO_3)_2$
(Plumbi Nitras U. S. P.).

Dissolve as much of the crystallized salt as the point of a knife blade will hold in a test tube full of water by the aid

of heat. This solution, diluted with 1 vol. of water, will give the following reactions:

Reactions for the Base. *1. **Hydric Sulphide** (6-8 vols.), *black lead sulphide*, PbS. The same reagent, however, may also produce a red precipitate: Add a few drops of HCl to some of the lead solution, and, if a white precipitate ($PbCl_2$) should form, dissolve it by the aid of heat. From this solution a few drops of H_2S will precipitate *red* $PbCl_2+3PbS$, which, on further addition of H_2S, will be converted into black PbS. Warm the liquid with the PbS precipitate, allow the latter to subside, and decant the supernatant liquid. To one part of the precipitate add a few (4-5) drops of nitric acid, to another part a few drops of hydrochloric acid, and boil. The precipitate dissolves in HNO_3 with the separation of sulphur, but remains unchanged in HCl.

2. **Ammonic Sulphide** produces the same precipitate. PbS.

3. **Sodic or Potassic Hydrate,** *white hydroxide*, $Pb(OH)_2$, which dissolves on warming with more of the alkali.

4. **Sodic Carbonate,** *white basic lead carbonate* (white lead, Plumbi Carbonas U. S. P.).

*5. **Sulphuric Acid dil.,** white *lead sulphate*, $PbSO_4$, which, on the addition of several drops of HCl or HNO_3, remains undissolved. If the solution contains ammonic salts or very much free acid the $PbSO_4$ will separate out only after the addition of alcohol (no chemical change, only physical insolubility).

*6. **Hydrochloric Acid or a Chloride,** white lead chloride, $PbCl_2$. Add NH_4OH to one-half of the precipitate; it remains unchanged (comp. **IX.**, 5, **XVI.**, 4). Heat the other half with half a test tube full of water. The $PbCl_2$ will dissolve, but on cooling crystallize out again in shining needles.

7. **Potassic Iodide** (6-10 drops) throws down yellow *lead iodide*, PbI_2. Fill the test tube with water, heat to boiling and

filter off quickly from the remaining PbI_2. The dissolved PbI_2 crystallizes out on cooling in glistening gold-yellow scales.

8. **Potassic Dichromate** (a few drops), yellow *lead chromate*, $PbCrO_4$ (chrome yellow), which dissolves on the addition of sodic hydrate (especially upon warming), but is not dissolved by dilute HNO_3.

9. Fill a test tube with a diluted solution of the lead salt and suspend in it a strip of a zinc sheet. Metallic lead will be precipitated on the zinc strip in the form of glistening scales or leaves (lead tree).

Reactions for the Acid.

*10. **A Copper turning** and several drops of conc. sulphuric acid, on being heated with some of the lead solution, evolve red fumes, which are recognized by their smell and color as NO_2. (The precipitate produced by the H_2SO_4 does not interfere with the reaction.)

*11. Add a few drops of indigo solution and some HCl to 8-10 drops of the lead solution. The mixture will be decolorized on heating.

Blowpipe Reaction.

*12. Fuse some of the lead salt with sodic carb. on charcoal before the blowpipe. A yellow deposit is formed beyond the fusion, and the latter contains soft, malleable globules of lead. Lead melts very easily before the blowpipe, and deposits a yellow coating of PbO (litharge, Plumbi Oxidum U. S. P.).

VI. RED LEAD, MINIUM=Pb_3O_4.

Warm a little of the red powder with *water*. It remains undissolved and unchanged.

*1 Take the point of a penknife full of minium and heat with HCl (10-12 drops). Cl gas will be evolved and the minium converted into white $PbCl_2$, which is soluble in a large quantity of warm water.

2. Dilute 1 vol. *nitric acid* with 4 vol. water and pour this dilute acid on a penknife-point full of minium in a test tube. It will be partly dissolved, especially on heating. A residue of brown dioxide, PbO_2, is left, which will quickly settle to the bottom. The supernatant liquid contains *nitrate of lead* and gives all the reaction of lead (comp. **V.**).

3. Heat a little minium in a glass tube; it will be converted into litharge (pale yellow when cold) and give off oxygen gas.

4. Minium, before the blowpipe on charcoal, is reduced to lead globules.

VII. BISMUTH.

Heat a knife-point full of the pulverized metal with a little conc. HNO_3. Continue heating with the occasional addition of small portions of conc. HNO_3, until *almost* all of the metal has dissolved. This solution of

Bismuth Nitrate = $Bi(NO_3)_3$,

which should not be diluted with water, gives the following reactions:

Reactions for the Base. *1: **Water** (8-10 vols.) precipitates white *basic nitrate*, $Bi(NO_3)(OH)_2$ (Bismuthi Subnitras U. S. P.). If previously several drops of conc. sol. of *sodic* or *ammonic chloride* have been added to the bismuth solution, water precipitates bismuth *oxychloride* (pearl white), Bi OCl, which is insoluble on addition of tartaric acid (comp. **XI.**, 1.) If the bismuth solution contains too much free acid, even a very large quantity of water will not produce a precipitate. (The amount of water necessary to sufficiently decrease the activity of the liquid for a precipitation of basic salt is, at the same time, sufficient to dissolve most or all of the latter, in spite of its being only slightly

soluble. For this reason any excess of acid in preparing the bismuth solution should be avoided).

*2. **Hydric Sulphide,** dark brown *bismuth sulphide,* Bi_2S_3.

3. **Ammonic Sulphide** the same; insoluble in excess of the reagent.

4. **Sodic, Potassic or Ammonic Hydrate,** *white hydroxide,* $Bi(OH)_3$, insoluble in excess of the precipitants (comp. V., 3).

5. **Ammonic Carbonate,** *white basic carbonate,* Bi_2CO_5 $(=(BiO)_2CO_3)$ (Bismuthi Subcarbonas U. S. P.).

6. **Potassic Dichromate,** *yellow chromate,* $Bi_2Cr_2O_9$, $(=(BiO)_2Cr_2O_7)$, soluble in dil. HNO_3, but insoluble in NaHO or KHO (comp. V., 8).

Blowpipe Reaction. 7. Bismuth melts before the blowpipe and gives a dark yellow coating and a *brittle* metallic globule (compare lead).

VIII. BARIC CHLORIDE=$BaCl_2$+2aq.

Dissolve a knife-point full of the salt in a test tube full of water by the aid of heat. This solution gives the following reactions:

Reactions for the Base. 1. **Hydric or Ammonic Sulphides or Ammonic Hydrate** nothing.

*2. **Ammonic or Sodic Carbonate,** white baric carbonate, $BaCO_3$.

*3. **Sulphuric Acid** dil. or a sulphate precipitates, even from a very dilute solution, *white baric sulphate,* $BaSO_4$, insoluble on addition of HNO_3 or HCl.

*4. **Calcic Sulphate** sol. (5-6 vols.) gives immediately *a white turbidity* of $BaSO_4$.

5. **Sodic Hydric Phosphate** precipitates $BaHPO_4$, soluble in HCl.

6. **Ammonic Oxalate,** *white baric oxalate,* BaC_2O_4.

7. **Potassic Chromate** (or dichromate, made alkaline by

NH_4HO), *yellow baric chromate*, $BaCrO_4$, soluble on addition of few drops of HNO_3 or HCl (comp. V., 8, VII., 6).

Reaction for the Acid. *8. **Argentic Nitrate**, *white, curdy* AgCl; the precipitate collects on shaking; it is insoluble in HNO_3 (several drops), but dissolves readily in NH_4HO (several drops).

9. Heat some baric chloride in a glass tube; it gives off its water of crystallization.

Blowpipe Reaction. 10. It melts on charcoal before the blowpipe; the fused mass, placed on red litmus paper and moistened with one drop of water, gives an alkaline reaction.

11. *Dip the hot loop of a platinum wire into the pulverized salt, and then introduce it into the flame of a Bunsen burner or a spirit lamp. The colorless flame will turn *yellowish-green.*

IX. MERCURY.

Dilute a little nitric acid (conc.) with the same volume of water and gently warm a few drops of mercury with this dil. acid; the metal will dissolve to *mercurous salt* with the liberation of brown fumes. To obtain a solution perfectly free from mercuric salt it is necessary that about half of the mercury remain undissolved, after the action of the acid is over (when large gas bubbles are colorless). Dilute this turbid solution of

Mercurous Nitrate $= Hg_2(NO_3)_2$.

with 5-6 vol. of water, allow to settle and use the decanted liquid for the following reactions:

Reactions for the Base. *1. **Copper**—*metallic mercury.* Dip a copper turning or a small, bright piece of copper sheet or wire into the diluted solution (1 drop sol., 10 drops water), taking

care, however, that only part of the copper be immersed, it becomes white, amalgamating as far as it dips under the liquid. Brighten the amalgamated part by gently rubbing it with a small piece of filter paper. The mercury will volatize and the copper reassume its red color if the amalgamated metal is heated in a flame.

*2. **Hydric or Ammonic Sulphide,** *black mercurous sulphide,* Hg_2S; the precipitate is insoluble in warm dil. HNO_3, as well as in ammonic sulphide.

*3. **Sodic or Potassic Hydrate,** *black mercurous oxide,* Hg_2O. (Lime water, calcic hydrate produces the black-wash of U. S. P.)

4. **Ammonic Hydrate** throws down a *black amido compound.* (In the presence of HCl or chlorides $(NH_2Hg)Cl$).

*5. **Hydrochloric Acid or a Chloride,** *white mercurous chloride,* HgCl (Calomel, Hydrargyrum Chloridi mite U. S. P.) which is turned black by addition of NH_4OH (comp. **VI.,** 6, and **XXI.,** 4).

6. **Potassic Iodide** (a few drops), *greenish-yellow mercurous iodide,* HgI. (Hydrargyri Iodidum Viride, U. S. P.)

7. **Potassic Dichromate,** *red mercurous chromate,* Hg_2CrO_4.

8. Dissolve the residue of mercury (left from above) to *mercuric nitrate* by warming with some HNO_3 conc. This solution still contains more or less mercur*ous* nitrate. In order to complete the oxydation, boil with the occasional addition of small quantities of HNO_3 conc., until a drop of the solution, diluted with water, does not react, *i. e.,* become turbid on the addition of a drop of HCl. This solution of

Mercuric Nitrate $= Hg(NO_3)_2$

(Hydrargyri Nitras U. S. P.)

diluted with 5-6 vols. of water, gives the following reactions:

Reactions for the Base.

*8. **Copper,** *metallic mercury*; same as for mercurous solution.

*9. **Hydric (or Ammonic) Sulphide** (drop by drop, shaking between successive additions) first white $Hg(NO_3)_2+2HgS$; as more and more H_2S is added the precipitate turns yellow, orange, brownish, and is finally converted into black, pure mercuric sulphide, HgS, by an excess of the reagent. Mercuric sulphide does not dissolve in dilute warm HNO_3.

*10. **Sodic or Potassic Hydrate** precipitates *yellow mercuric oxide*, HgO. (Hydrargyri Oxidum Flavum U. S. P.; lime water would produce yellow wash U. S. P.)

11. **Ammonic Hydrate** (a few drops), a *white amido compound* $(NH_2Hg)NO_3$ (compare Hydrarg. Ammoniatum U. S. P.) In the presence of large quantities of ammonic salts (from too much free acid in the mercuric nitrate sol.) the precipitate either does not form or dissolves in the excess of NH_4OH.

12. **Sodic Carbonate,** brownish-yellow basic carbonate.

13. **Hydrochloric Acid,** no change.

14. **Potassic Iodide** (add by drops) *scarlet-red mercuric iodide*, HgI_2 (Hydrarg. Iodid. Rubrum U. S. P.) soluble in excess of precipitant.

15. **Potassic Dichromate,** yellowish-red mercuric chromate.

16. Mix a little of a dry mercury compound with anhydrous sodic carb. and a little charcoal powder and heat the mixture in a glass tube. A mirror, composed of minute drops of mercury, will be deposited on the sides of the tube. The metallic nature of the deposit becomes apparent on rubbing the globules together with a splinter of wood or a match.

X. TIN.

Warm some granulated tin or a few tin turnings for quite a long time with conc. HCl until the liberation of hydrogen gas has ceased and the greater part of the metal

has been dissolved. Heat gently, to avoid the boiling away of the HCl. The solution contains

Stannous Chloride = $SnCl_2$

and gives the following reactions:

Reactions for the Base. *1. **Hydric Sulphide,** *dark-brown stannous sulphide,* SnS. Warm the fluid with the precipitate in it for quite a while, and allow it to stand several minutes until the precipitate has settled to the bottom. Decant the supernatant liquid as much as possible and *warm* (not boil) the precipitate with 10-12 drops of yellow ammonic sulphide. The stannous sulphide will dissolve to ammonic sulphostannate after being converted into *first* stannic sulphide. The latter may be obtained as a yellow precipitate on the addition of HCl to the well diluted sulphostannate solution.

*2. **Ammonic Sulphide** (a few drops) produces the same precipitate.

3. **Sodic Hydrate,** *white stannous hydrate,* $Sn(OH)_2$, soluble in excess of the alkali.

4. **Sodic Carbonate,** *stannous hydrate,* $Sn(OH)_2$ CO_2 escapes.

5. **Mercuric Chloride [or Nitrate]** (2-3 drops) either white *calomel* (Hg_2Cl_2), or gray *metallic mercury* and stannic chloride, $SnCl_4$.

Boil the remainder of the tin with HNO_3. The metal will be converted into white metastannic acid, $H_{10}Sn_5O_{15}$, without being dissolved.

Dissolve completely a little gran. tin in the least possible quantity of aqua regia (1 vol. HNO_3+3 vols. HCl) by heating. Use fresh quantities of acid only when the liquid gets turbid or the metal no more decreases. This solution contains *stannic* and *stannous* chloride. Complete the oxydization by adding a few drops of HNO_3 conc. and heating

until a drop of the liquid, diluted with some water, gives a *light yellow* precipitate with H_2S. This solution which contains exclusively

Stannic Chloride=$SnCl_4$,

diluted with 5-6 vols. of water, gives the following reactions:

Reactions for the Base.

*6. **Hydric Sulphide** (8-10 vols.), *yellow stannic sulphide*, SnS_2, soluble in ammonic sulphide. Add HCl to this well diluted solution and the precipitate will reappear (comp. X., 1). To a portion of the stannic solution first add about 3 vols. of a saturated solution of oxalic acid and then H_2S, *no precipitate* is formed. If less oxalic acid is used, H_2S colors the solution yellow and a precipitate will form after a time, more rapidly on warming.

*7. **Ammonic Sulphide** (several drops to the very dilute solution) produces the same precipitate.

8. **Sodic Hydrate,** *white stannic hydrate*, H_2SnO_3, soluble in excess of alkali to *sodic stannate*, Na_2SnO_3.

Blowpipe Reaction.

9. Tin is easily fusible before the blowpipe and burns to white SnO_2.

XI. ANTIMONY.

Heat a small portion of the pulverized metal with HCl; it remains unchanged. Boil another small portion with HNO_3; the metal is converted into white oxide, but not dissolved.

Warm a penknife-point full of pulverized antimony with several drops of aqua regia (1 vol. HNO_3, 3 vols. HCl) and add as much of the mixture as is required to dissolve *almost* all of the metal. This solution of

Antimony Trichloride=$SbCl_3$,

which should not be diluted with water, gives the following reactions:

Reactions for the Base. *1. **Water** (8-10 vols.), *white oxychloride*, SbOCl (powder of algaroth), tartaric acid, if previously added, prevents the precipitation by water (comp. **VII.**, 1).

*2. **Hydric Sulphide** precipitates *orange-yellow* antimony trisulphide, Sb_2S_3 (Antimonii Sulphidum U. S. P.), which dissolves in yellow ammonic sulphide (comp. **X.**, 1) to sulphantimonite and sulphantimonate. Hydrochloric acid precipitates from this well diluted solution a mixture of Sb_2S_3 and Sb_2S_5 (golden sulphuret) oxalic acid does not prevent precipitation by H_2S.

3. **Ammonic Sulphide** produces the same precipitate as H_2S.

4. **Sodic Hydrate,** *white antimonous hydrate*, $HSbO_2$, soluble in excess of precipitant.

5. **Ammonic Hydrate** gives $HSbO_2$, insoluble in excess. Previous addition of tartaric acid prevents precipitation.

Blowpipe Reactions. 6. Antimony melts in a glass tube without volatilizing.

*7. It melts on charcoal before the blowpipe and evolves copious heavy fumes of antimonous oxide, Sb_2O_3, which deposits a *white coating* on the charcoal which crystallizes around the bead on cooling. Fuse a piece of Sb the size of a match-head before the blowpipe on charcoal and while very hot quickly throw it out on the table. It spatters and the small globules formed, in running out, leave white tracks, from Sb_2O_3, in their wake.

XII. ARSENIOUS ANHYDRIDE=As_2O_3.

(White arsenic, Acidum Arseniosum U. S. P.)

Warm a penknife-point full of white arsenic in a test tube full of water for quite a time (10 min.). A solution is obtained which will scarcely redden blue litmus paper. It gives the following reactions:

Reactions for the Base. *1. **Hydric Sulphide** (8-10 vols.) only turns the solution yellow. From this liquid, however, addition of a few drops of HCl will throw down *yellow arsenic trisulphide*, As_2S_3, which dissolves readily in ammonic sulphide or carbonate. Yellow As_2S_3 is re-precipitated from these (well diluted) solutions on supersaturating them with HCl. Previous addition of oxalic acid *does not* prevent the precipitation of arsenic by H_2S (comp. X., 6).

*2. **Ammonic Sulphide** (2-4 drops) will not precipitate anything. An addition of HCl is necessary to precipitate As_2S_3.

3. **Argentic Nitrate** (2-3 drops), no reaction. Neutralize the arsenious acid with 1 drop of NH_4OH and a *yellow* precipitate of *argentic arsenite*, Ag_3AsO_3, is produced. It is readily soluble in both free NH_4OH and HNO_3.

4. **Cupric Sulphate** (2-3 drops), no precipitate. Addition of 1 drop of NH_4OH will throw down *green cupric arsenite*, $CuHAsO_3$ (Scheele's green), which dissolves with *blue color* in more of the NH_4OH.

5. Metallic arsenic dissolves on being boiled with aqua regia. Heat some As in a closed glass tube; it volatilizes without melting previously, and deposits a mirror of the metal.

Blowpipe Reactions. *6. Heat a very small quantity of As before the blowpipe on charcoal. It burns to *white* As_2O_3, with the formation of a garlic-like odor (due to fumes of metallic arsenic).

*7. Place some As_2O_3 (the size of a pin-head) into the bottom of a closed glass tube, and some powdered charcoal on top of it. Heat very slowly from top downward, and a mirror of As will be deposited above the charcoal.

8. As_2O_3 on charcoal before the blowpipe gives white fumes and garlic-like odor.

XIII. POTASSIC ALUMINIC SULPHATE=$K_2Al_2(SO_4)_4 + 24aq$.

(Alum. Alumen U. S. P.).

Dissolve a large knife-point full of the salt in a test tube full of water by the aid of heat. It dissolves readily in hot, but with great difficulty in cold water. The solution reddens blue litmus paper and gives the following reactions:

Reactions for the Base.

1. **Hydric Sulphide** nothing.

*2. **Ammonic Sulphide** (3-4 drops), white, pasty gelatinous *aluminic hydrate*, $Al_2(OH)_6$, with the liberation of H_2S.

*3. **Sodic Hydrate** (only a few drops), the same precipitate. Add more alkali and the precipitate will dissolve. Divide this solution of *sodic aluminate*, $Na_6Al_4O_9$, into 2 parts, and add to one ammonic chloride, to the other hydric sulphide. Ammonic chloride decomposes the aluminate and reprecipitates *aluminic hydrate*, whilst hydric sulphide has no effect. (Comp. **II.**, 3.)

*4. **Ammonic Hydrate** gives *aluminic hydrate*, insoluble in excess of precipitant. If tartaric acid is added to a solution of alum, neither sodic, potassic nor ammonic hydrate will produce a precipitate.

5. **Sodic Carbonate** precipitates *aluminic hydrate* with the liberation of carbonic acid gas.

6. **Sodic Hydric Phosphate** throws down white *aluminic phosphate* which dissolves in excess of sodic hydrate, but is insoluble in ammonic hydrate, except in presence of tartaric acid (comp. 3 and 4).

Reaction for the Acid.

7. **Baric Chloride** gives basic sulphate (comp. **I.**, 9).

Blowpipe Reaction.

8. Alum upon being heated in a glass tube gives off water.

9. Fuse a little alum with 6 parts of sod. carb. before the blowpipe on charcoal. The fusion blackens moist silver.

10. *Introduce a small piece of the salt on platinum wire into a Bunsen or spirit lamp flame. The flame becomes *violet*, potassium flame.

XIV. CALCIC CARBONATE=$CaCO_3$.

Marble, Limestone, Chalk.

Calcic carbonate is insoluble in water, but dissolves in hydrochloric acid, with the liberation of a colorless and odorless gas: carbonic anhydride, CO_2. In order to obtain a neutral solution, warm a piece of marble the size of a bean with hydrochloric acid until the evolution of gas has ceased. Finally heat to boiling in order to expel the carbonic acid gas absorbed by the liquid. Take, however, only as much acid as will leave some of the marble undissolved. A burning splinter of wood will be extinguished if plunged into the upper part of the test tube during the evolution of CO_2.

When all of the carbonic acid gas is expelled, dilute with water; this is a neutral solution of

Calcic Chloride=$CaCl_2$

(Calcii Chloridum U. S. P.).

It gives the following reactions with:

Reactions for the Base.

1. **Hydric or Ammonic Sulphide** nothing.
2. **Ammonic Hydrate** nothing.

*3. **Ammonic or Sodic Carbonate,** *white calcic carbonate*, $CaCO_3$. (Calcii Carbonas Præcip. U. S.)

*4. **Sulphuric Acid,** dil. *white calcic sulphate*, $CaSO_4+2aq$. (Gypsum). No precipitate will form, however, if the calcic solution is largely diluted with water previous to adding sulphuric acid. If half vol. of alcohol is added to this solution of calcic sulphate, the precipitate will separate out at once upon shaking (comp. **VIII.,** 3 and 4).

*5. **Ammonic Oxalate** throws down *calcic oxalate*, $CaC_2O_4 + 2aq$. The precipitate dissolves on addition of hydrochloric acid.

6 **Sodic Hydric Phosphate,** *white calcic phosphate*, $CaHPO_4 + 4aq$.

7. **Potassic Dichromate,** no precipitate in both neutral and ammoniacal calcic solutions (comp. **VIII.,** 7, and **XV.,** 5).

Blowpipe Reaction. 8. Ignite a small piece of marble, the size of a mustard seed, before the blowpipe on charcoal. CO_2 escapes and the residue has an *alkaline reaction, i. e.,* turns blue a piece of moist red litmus paper.

XV. STRONTIC CARBONATE=$SrCO_3$.

(Strontianite).

Insoluble in water, but soluble in hydrochloric acid with the liberation of carbonic acid, CO_2 (comp. **XIV.**).

This solution *strontic chloride*, $SrCl_2$ gives the following reactions:

Reactions for the Base. 1. **Hydric or Ammonic Sulphide or Ammonic Hydrate** nothing.

*2. **Sulphuric Acid,** dil. *white strontic sulphate*, $SrSO_4$. In very dil. solutions the precipitate appears only after shaking (comp. **VIII.,** 3 and 4).

*3. **Calcic Sulphate** solution renders the solution turbid only after some shaking.

4. **Sodic Hydric Phosphate** white *strontic phosphate*, soluble in hydrochloric acid.

5. **Potassic Dichromate** no precipitate in dilute ammoniacal solution (comp. **VIII.,** 7, and **XIV.,** 7).

*6. Dip a platinum wire in the strontic solution and introduce into the flame. It is *colored red.*

XVI. AMMONIC CHLORIDE=AmCl.

(Sal-ammoniac, Ammonii, Chloridum U. S. P.)

The solution has a neutral reaction.

Reactions for the Base. 1. **Hydric or Ammonic Sulphide, Ammonic or Sodic Carbonate,** produce no precipitate.

2. **Tartaric Acid** throws down from concentrate solutions white crystalline *Ammonic hydric tartrate,* $AmH(H_4C_4O_6)$. Shaking facilitates the formation of the precipitate, especially in case of a somewhat dilute solution. Precipitate soluble in hydrochloric acid and in sodic hydrate.

*3. Heat a small knife-point full of the salt with sodic hydrate. The gas discharged at the mouth of the test tube smells of *ammonia,* NH_3, and on coming into contact with moist red litmus paper, *colors it blue.*

Reaction for the Acid. *4. **Argentic Nitrate** precipitates AgCl (dilute solution previously). Precipitate soluble in ammonic hydrate; insoluble in nitric acid.

XVII. POTASSIC NITRATE=KNO_3.

(Nitre, Potassii Nitras U. S. P.)

Dissolve a knife-point full of the salt in a test tube half full of water. The solution has a neutral reaction.

Reaction for the Base. 1. **Tartaric Acid** (conc.) precipitates from it *potassic hydrate tartrate,* ($KHC_4H_4O_6$, cream of tartar) (Potassii Bitartrus U. S. P.) Precipitate dissolves in acids (hydrochloric) and in sodic hydrate (with the formation of Rochelle salt, $KNaH_4C_4O_6$).

Reactions for the Acid. *2. **A copper turning,** brought into the solution heated with conc. sulphuric acid, liberates reddish-brown fumes (comp. V., 10.)

*3. **Solution of Indigo** is discolored by heating with the solution which has been previously mixed with some hydrochloric acid (comp. V., 11).

4. Heat a small piece of nitre before the blowpipe on charcoal. The result is a violent deflagration. The residue

contains potassic carbonate and has an alkaline reaction, *i. e.*, colors red litmus paper blue.

5. Nitre fuses on being heated in a glass tube. Oxygen is evolved.

*6. Nitre colors a flame *violet: potassium flame.*

XVIII. MANGANESE DIOXIDE=MnO_2

(Mangani Oxidum Nigrum U. S. P.)

1. The mineral ground to a fine powder is insoluble in water and dil. sulphuric or nitric acid.

2. Boil a small portion of it with hydrochloric acid. It dissolves to *manganous chloride*, $MnCl_2$, with the liberation of chlorine. The solution, after filtering from the undissolved powder, may be used for repeating the reactions on manganese (comp. **III.**, 1-5).

3. Manganese dioxide is infusible before the blowpipe on charcoal.

4. Add an exceedingly small quantity of the mineral to a borax bead. It will be colored violet.

*5. Fuse a minute quantity of the mineral with sod. carb. and nitre on platinum foil. A green fusion is obtained (comp. **III.**). If too much of the manganese compound is used, the color is so intensely dark green that it appears black.

XIX. MAGNESIC SULPHATE=$MgSO_4+7aq$.

(Epsom Salts; Magnesii Sulphas U. S. P.)

Dissolve a large knife-point full of the salt in a test tube full of water with the aid of heat. The solution has an acid reaction.

Reaction for the Base. 1. **Hydric (or Ammonic) Sulphide** precipitates nothing.

2. **Sodic Hydrate** throws down *magnesic hydrate*, $Mg(OH)_2$.

*3. **Ammonic Hydrate** the same. If, however, ammonic chloride, or some other ammonic salt, has been added previously to the solution, *ammonic hydrate will not throw down anything* (comp. **II.**, 4). Hence, previous addition of any acid will likewise prevent a precipitation.

4. **Sodic Carbonate** throws down a *basic carbonate* which is soluble in ammonic salts (Magnesii Carbonas U. S. P.)

*5. **Ammonic Carbonate** nothing (comp. 3).

*6. **Sodic Hydric Phosphate** throws down a *crystalline precipitate* of *ammonic magnesic phosphate*, $MgAmPO_4+6aq.$, *from solutions containing ammonic chloride* (*or other ammonic salts*) *and ammonic hydrate.* In very dilute solutions the precipitate forms only on shaking.

Reactions for the Acid. *7. **Baric Chloride,** *baric sulphate*, $BaSO_4$, insoluble in HCl.

8. **Plumbic Acetate,** *plumbic sulphate*, insoluble in dil. acids (nitric).

On heating the salt in a glass tube water is given off.

XX. SODIC HYDRIC PHOSPHATE=$Na_2HPO_4+12aq.$

(Sodii Phosphas U. S. P.)

Dissolve a knife-point full of the salt in a test tube full of water.

The solution has an alkaline reaction and nothing is precipitated by tartaric acid, alkaline sulphides or carbonates. The solution gives the following reactions:

Reactions for the Acid. *1. **Argentic Nitrate,** *yellow tri-argentic phosphate*, Ag_3PO_4, and nitric acid. Precipitate readily soluble in both $(NH_4)OH$ and nitric acid.

2. **Plumbic Acetate,** white *tri-plumbic phosphate*, $Pb_3(PO_4)_2$, soluble in nitric acid, insoluble in $(NH_4)OH$.

3. To 1 drop of solution add ½ test tube full of water, a few drops of HNO_3 and then 10-12 drops of *ammonic molybdate.* The solution will turn *yellow upon heating,* and a yellow precipitate will form after standing awhile.

4. **Baric Chloride,** *baric phosphate,* $BaHPO_4$.

*5. **Magnesic Sulphate,** on *previous addition of ammonic chloride and hydrate,* throws down $MgAmPO_4+6aq$. If solution is very dilute the precipitate separates out only after shaking.

On heating the salt in a glass tube it gives off water.

*A colorless *flame becomes yellow* if sodic phosphate is introduced; *sodium flame.*

XXI. SILVER.

Dissolve a small silver coin in the least possible amount of *nitric acid* with the aid of heat. The blue solution contains the *nitrates of silver and copper.* Dilute it with a large amount of water and precipitate the silver as argentic chloride, by adding hydrochloric acid drop by drop, as long as a reaction takes place. The turbid liquid will clear up on shaking; the white, curdy precipitate settles rapidly; the supernatant clear liquid solution contains *cupric nitrate,* and when decanted from the AgCl, it may be used to repeat the reactions for copper (comp. **I.**). Fill the test tube or containing vessel with water, shake well and decant from the AgCl. Wash the precipitate two or three times more in the same manner, when all the cupric solution will be removed from the precipitate. Dissolve the washed AgCl by adding a *small* quantity of NH_4OH and immerse a little zinc into the solution. The AgCl will be reduced to *metallic* Ag after 24 hours. Remove the undissolved zinc and wash the metallic silver by repeatedly heating it with water (the first time previously acidulated with a little sulphuric acid). Finally, dissolve the pure silver by heating it with the least possible amount of HNO_3. The solution contains:

Argentic Nitrate=$AgNO_3$

(Argenti Nitras U. S. P.).

The diluted solution gives the following reactions:

Reactions for the Base.

1. **Copper** precipitates *crystalline metallic silver*. The solution turns blue from cupric nitrate, $Cu(NO_3)_2$. Dilute a few drops of the argentic solution and place a little piece of copper in it.

*2. **Hydric or Ammonic Sulphide,** *black argentic sulphide*, Ag_2S.

3. **Sodic Hydric Phosphate** (a few drops), yellow *tri-argentic phosphate*, Ag_3PO_4; dissolves readily in NH_4OH (a few drops) and in HNO_3; therefore, no precipitate is formed if the above solution contains free nitric acid.

*4. **Hydrochloric Acid or a Chloride,** *white, curdy* AgCl, which is blackened on exposure to the light. It dissolves readily in NH_4OH, but not in HNO_3 (a few drops) (comp. **V.**, 6, and **IX.**, 5).

5. **Potassic Iodide** (a few drops) *light-yellow argentic iodide*, insoluble on addition of HNO_3 or NH_4OH.

XXII. POTASSIC DICHROMATE=$K_2Cr_2O_7$.

Dissolve a crystal of the salt the size of a bean in ½ test tube full of water; divide the solution into 2 parts and dilute one of them with still more water. From this dilute solution there is precipitated by:

1. **Hydric Sulphide,** *grayish-green chromic hydrate*, $Cr_2(OH)_6$, mixed with sulphur. The solution contains (yellow) potassic chromate K_2CrO_4. Ammonic sulphide acts in the same way. If HCl is added to the original solution previous to the addition of H_2S, sulphur only will be thrown down. All the chromate is reduced to chromic salt, and the liquid turns green, especially upon heating.

Reactions for the Acid.

2. **Plumbic Acetate,** *yellow plumbic chromate,* $PbCrO_4$, soluble in KHO, insoluble in dil. HNO_3.

3. **Potassic, Sodic or Ammonic Hydrate or Sodic Carbonate** change the red color of the solution into yellow (formation of K_2CrO_4 from $K_2Cr_2O_7$).

4. Potassic Dichromate is readily reduced to chromic salt, *e. g.*, by H_2S in acid solution (comp. **I.**), or on addition of sulphurous acid sol. ($=H_2SO_3$) (to *potassic chromic sulphate*=chromic alum). Heat the second part of original solution with several drops of hydrochloric acid. Add alcohol drop by drop and keep the liquid warm. A fruity odor is given off; the chromate is reduced and the emerald green liquid contains:

Chromic Chloride=Cr_2Cl_6.

Reactions for the Base.

5. **Hydric Sulphide** precipitates nothing.

*6. **Ammonic Sulphides** throw down *grayish-green chromic hydrate,* $Cr_2(OH)_6$.

*7. **Sodic Hydrate,** *chromic hydrate,* which dissolves with green color on the addition of more of the alkali. Boiling will reprecipitate the chromic hydrate.

8. **Ammonic Hydrate** produces the same precipitate, ($Cr_2(OH)_6$) which after long standing (in excess of NH_4OH), will dissolve more or less with a reddish violet color.

9. **Sodic Carbonate,** *greenish-gray, basic carbonate.*

Blowpipe Reaction.

*10. Fuse a small particle of potassic dichromate or some other chromium compound in a borax bead. It will be *colored emerald green.*

*11. Filter off precipitate obtained with sodic carbonate and fuse some of it on platinum foil with sod. carb. and nitre. The fusion is *colored yellow* with K_2CrO_4.

*12. Boil some conc. solution of a chromate with conc. hydrochloric acid. Chlorine is evolved and Cr_2Cl_6 is formed.

XXIII. SODIC TETRABORATE=$Na_2B_4O_7+10aq$.

(Borax, Sodii Boras U. S. P.)

Dissolve a piece of borax the size of a bean in a test tube one-half full of water. The solution has an alkaline reaction.

Reaction for the Acid. 1. **Conc. Hydrochloric or Suphuric Acid** throws down boric acid, H_3BO_3 (Acidum Boricum U. S. P.) as the liquid cools the precipitate will become more copious.

2. **Baric Chloride,** *baric borate,* BaB_2O_4, soluble in much water, especially upon heating.

Borax gives off water on being heated in a glass tube.

*3. Introduce borax into the flame by means of a platinum wire; it bubbles and swells up and finally melts to a clear bead (=*borax bead*). The flame shows the yellow *sodium color* during this process.

*4. Moisten a borax bead with a drop of conc. sulphuric acid and introduce it into the *edge* of the flame. At first the flame is colored *green from boric acid,* later on sodic salt is volatilized and its yellow color prevails (comp. **VIII.,** 11).

XXIV. POTASSIC IODIDE=KI.

(Potassii Iodidum U. S. P.)

Dissolve a piece of the salt the size of a bean in a test tube full of water. From this solution there is precipitated by:

Reactions for the Acid. *1. **Plumbic Acetate,** *yellow plumbic iodide,* PbI_2, soluble in a large amount of hot water. Crystallizes out on cooling (comp. **V.,** 7).

2. **Mercuric Chloride or Nitrate,** *scarlet red,* HgI_2, (comp. **IX.,** 14.)

*3. **Argentic Nitrate,** *yellow argentic iodide,* AgI, insoluble in HNO_3 and NH_4OH.

*4. **Starch Paste** and a drop of dil. fuming nitric acid color the very dilute solution a *deep blue.* This blue color disappears on heating but reappears on cooling. Instead of fuming nitric acid 1 drop of HCl and 1 drop potassic permanganate, $K_2Mn_2O_8$, may be used.

5. Potassic iodide, on being fused with the addition of a minute piece of potassic dichromate, gives off *violet vapors* of Iodine. The same effect is obtained by heating potassic iodide with a little manganese dioxide and H_2SO_4 conc.

6. The Bunsen flame is *colored violet* by the salt=*potassium flame.*

XXV. CADMIC SULPHATE=$CdSO_4$+4aq.

Dissolve a piece of the salt the size of a bean in a test tube full of water by the aid of heat. This solution gives the following reactions:

Reactions for the Base. 1. **Zinc,** *metallic cadmium* (comp. **V.,** lead-tree).

*2. **Hydric Sulphide,** *yellow cadmic sulphide,* CdS.

3. **Ammonic Sulphide** the same precipitate, insoluble in excess of ammonic sulphide (comp. **X.,** 6, and **XII.,** 1).

*4. **Sodic Hydrate,** *white cadmic hydrate,* $Cd(OH)_2$, insoluble in more alkali (comp. **I.,** 4, and **XIX.,** 3.)

*5. **Ammonic Hydrate** the same; insoluble in excess of precipitant. Ammonic hydrate (or carbonate), however will form no precipitate in cadmic solutions if a large quantity of an ammonic salt has been previously added (comp. **II.,** 4). Sodic hydrate precipitates cadmic hydrate from the ammoniacal cadmium solution, even in the presence of ammonic salts. Warming facilitates this reaction.

6. **Ammonic Carbonate,** *white cadmic carbonate,* $CdCO_3$, insoluble in excess of precipitant.

Reaction for the Acid. 7. **Baric Chloride,** *baric sulphate,* $BaSO_4$.

8. Fuse some of the salt with dry sod. carb. on charcoal before the blowpipe. A rainbow-colored coating of CdO is deposited on the charcoal without the formation of metallic globules (comp. **II.** and **V.**).

XXVI. NICKEL SULPHATE=$NiSO_4$+7aq.

The green solution of the salt reacts as follows:

Reactions for the Base.

1. **Hydric Sulphide,** no reaction.

*2. **Ammonic Sulphide,** *black nickel sulphide,* NiS, which is insoluble in dil. hydrochloric and in acetic acids.

3. **Sodic Hydrate,** *pale green hydroxide,* $Ni(OH)_2$.

4. **Ammonic Hydrate** the same precipitate, soluble in more NH_4OH with pale blue color.

*5. **Sodic Carbonate,** *apple-green basic carbonate.*

6. **Ammonic Carbonate** the same; the precipitate is soluble in excess of ammonic carbonate, with a *bluish-green color.*

7. The salt loses water on being heated in a glass tube.

8. The fusion obtained with sod. carb. before the blowpipe on charcoal blackens moist silver.

9. The borax bead is *colored reddish-brown* by a little fragment of the salt.

XXVII. COBALT SULPHATE=$CoSO_4$+7aq.

The reddish solution reacts as follows:

1. **Hydric Sulphide,** no reaction.

*2. **Ammonic Sulphide,** *black cobalt sulphide,* CoS, insoluble in dil. HCl.

3. **Ammonic Hydrate,** a *blue basic salt*; after some time it dissolves with a brown color in excess of NH_4OH.

4. **Sodic Carbonate,** *a basic carbonate.*

*5. **Ammonic Carbonate,** a basic salt of *peach blossom color*; it is soluble in an excess with a violet-red color.

6. **Sodic Hydric Phosphate,** *violet-blue phosphate,* $Co_3(PO_4)_2$.

*7. The salt, even in minute quantities, *colors the borax bead blue.*

XXVIII. IRON PYRITES=FeS_2.

1. Warm a small knife-point full of the pulverized mineral with HCl; it *remains unchanged.* Boil a similar portion with HNO_3; it *dissolves* with the liberation of reddish-brown fumes and the separation of gray flakes of sulphur.

This solution, diluted with water, shows all the reactions for ferric compounds (**IV.**, 7–14) *and* H_2SO_4.

2. *Heat strongly* a little of the powder in a glass tube; sulphur sublimes and the residue is *soluble in HCl* with the liberation of H_2S. The latter is recognized by its smell and its action (blackening) on filter paper moistened with lead acetate solution.

3. *Ignite* a small piece of pyrites before the blowpipe on charcoal. It burns with a pale blue flame which smells of SO_2. The residue fuses and is then *soluble in HCl* with the evolution of H_2S. If the test is *fused for a long* time it is *converted into magnetic oxide of iron,* Fe_3O_4.

4. A sample of the pulverized mineral with dry sod. carb. before the blowpipe on charcoal gives a fusion which blackens moist silver.

XXIX. HEAVY SPAR=$BaSO_4$.

The finely pulverized mineral is insoluble in water and in all acids.

1. Boil a knife-point full for a long time with a saturated solution of Na_2CO_3. Na_2SO_4 and $BaCO_3$ are formed. Filter off the residue, wash it out and pour dilute warm HCl on the filter. *The $BaCO_3$ dissolves in the acid and the filtrate contains $BaCl_2$ and gives the reactions of* **VIII.**

2. The liquid obtained by boiling the powder with Na_2CO_3 contains, besides the latter, Na_2SO_4. *Acidulated with HCl, it gives the reactions for sulphuric acid* (comp. **I.**, 9).

3. Fuse some of the baric sulphate with dry sod. carb. on charcoal. The fusion contains Na_2S, which blackens moist silver (comp. **I.**).

PART II.

SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.

In examining any substance for its various constituents certain reagents must be used systematically. Only by so doing is it possible to state with certainty that the substance under investigation contains certain constituents and that others are not present. It is not by any means sufficient to show that this or that element is present, but it is just as *necessary to prove that only these and no others are present.*

The work of examining a given substance is divided into two parts, viz.: examination for *bases or electropositive* and *acids or electronegative* constituents. The determination of the bases is to preceed the examination for acids. In examining for the latter, *first consider which of the acids may be present, taking into account the constituents and properties of the substances already determined.*

PAY SPECIAL ATTENTION TO THE FOLLOWING POINTS:

1. In substances soluble in water you cannot expect to find an acid, which forms a compound, insoluble in water, with one of the bases determined: thus, *e. g.*, the presence of a heavy metal or metal of the alkaline earths in a substance soluble in water will exclude the presence of carbonic, phosphoric or boric acid; or, barium or lead being present in a substance soluble in water or hydrochloric acid, there is no necessity to test for sulphuric acid.

2. Be careful that the reagent intended to detect the acid may not give a precipitate with one of the metals present; *e. g.*, in testing a silver-bearing substance for sulphuric acid one ought not to use baric chloride as a reagent, because its chlorine would give a precipitate just as well with the silver as the barium would with the sulphuric acid. In this case baric nitrate should be used instead of baric chloride or the silver should be removed by hydrochloric acid before adding the baric chloride.

3. Be careful not to test a substance for constituents which have been introduced as reagents during previous tests, *e. g.*, don't test a substance dissolved in hydrochloric acid for chlorine. Substances to be tested for chlorides should not be dissolved in hydrochloric but in nitric acid.

4. In testing a solution, first add but a few drops of the reagent, and a little more only if a precipitate is obtained.

5. Never add ammonic sulphide or carbonate to a solution containing free acid, but first ammonic hydrate to perfect neutrality (until liquid smells of ammonia after shaking), no matter whether this addition causes a precipitate or not.

6. In testing a solution with hydric sulphide sol. use at least 5 vols. of the latter. Ammonic sulphide, however, should be added, drop by drop, only, to the liquid previously neutralized with ammonic hydrate.

In order to examine any substance, heat no more than a small knife-point full with about $\frac{1}{3}$ test tube full of water; if this does not dissolve the substance at all, or only partially, heat another portion equally as large with 10-15 drops of hydrochloric acid and then add a little water. If the above fails to produce a solution, try a third portion with nitric acid. *But always avoid excess of acids.* If even now the substance does not dissolve it has to be regarded as insoluble in

water and acids. Accordingly it will be practical to divide all substances into 3 classes, viz.: Those

SOLUBLE IN WATER,
SOLUBLE IN ACIDS ONLY,
INSOLUBLE IN WATER AND IN ACIDS.

Sometimes a substance will not be dissolved by either water or acids, but will be changed; a fact which should be carefully noted, as it may give a valuable hint for the detection of certain constituents.

DETECTION OF THE BASES.

The bases with regard to their behavior towards the most important reagents may be divided into 5 groups. The CHIEF REAGENTS are the following four:

1. **Hydric Sulphide.** 2. **Ammonic Sulphide.** 3. **Ammonic Carbonate.** 4. **Sodic Hydric Phosphate.**

The following table shows, at a glance, the classification into 5 groups. From the solution, acidulated with a few drops of hydrochloric acid, there is precipitated by:

Hydric Sulphide		*Ammonic Sulphide	Ammonic Carbonate	Sodic Hydric Phosphate	Not Precipitated.
Precipitate is, in Am_2S,		Fe	Ba	Mg	K
		Co	Sr		Na
Soluble	Insoluble	Ni	Ca		Am
Sb	Hg	Mn			
As	Pb	Cr			
Sn	Ag	Zn			
	Cu	Al			
	Bi				
	Cd				

These reagents, as well as those given later on, are to be used in invariably the same order, and the following re-

*Add first NH_4OH to alkaline reaction.

agent is only to be used if the preceding one either gave on precipitate, or if all the precipitable matter has been thrown down by it and filtered off.

Before starting on the examination in the wet way, it is very useful to make a few blowpipe tests. These so-called preliminary tests often give important hints, in many cases prove the presence of certain substances with perfect distinctness, or, at least, make their presence probable.

PRELIMINARY TESTS.

1. Heat a sample of the substance (the size of a pinhead) in a glass tube, and see whether there is any sublimate to be distinguished or water escaping.

2. Ignite in a glass tube a quantity equally as large with anhydrous sodic carbonate and charcoal powder. (If the substance contains water, remove it by previously heating moderately and cautiously on platinum foil.) The formation of a metallic ring is an indication of arsenic or mercury (see †**IX.** and **XII.**).

3. Heat a small quantity of substance on charcoal before the blowpipe. There may be a deflagration, a characteristic smell or a coating (comp. **XVII.**, **XII.**, **V.**).

4. Heat a small quantity of substance with dry sod. carb. before the blowpipe on charcoal and observe: coating, metallic globules and fused mass (comp. **I.**, **III.**, **V.**, **VI.**, **VII.**, **XXV.**).

After having detected by the aid of the following scheme, the constituents of a substance, it is very useful to make several confirmatory tests, such as are given in the "REACTIONS." For this reason in the subsequent chapter, when an element is indicated, reference is made to the corresponding number in the "REACTIONS."

†Subjects under Part I., "Reactions."

CHAPTER I.

SECTION 1.

EXAMINATION OF SIMPLE SUBSTANCES.

(CONTAINING AT MOST 1 BASE AND 1 ACID.)

COMPOUNDS SOLUBLE IN WATER.

A. Bases.

OUTLINES OF THE PROCESS.

Dissolve a small knife-point full of the substance to be examined in a test tube one-third full of water, with the aid of heat.

Add some 6 or 8 drops of hydrochloric acid to about one-quarter of above solution (a precipitate thus formed would indicate a lead, silver or mercurous salt) and then, no matter whether hydrochloric acid has produced a precipitate or not, add:

Hydric Sulphide.

If a precipitate is formed examine it according to (*page 78*) ..... **I.**

If hydric sulphide produced no precipitate add to a second portion of original solution some ammonic chloride and ammonic hydrate until the fluid smells of it after shaking; and, no matter whether ammonic hydrate produced a precipitate or not, add a few drops of

Ammonic Sulphide.

If a precipitate is formed, examine it according to (*page 82*) ..... **II.**

If also ammonic sulphide produces no precipitate, add to a third portion of original solution ammonic chloride and ammonic hydrate and

Ammonic Carbonate.

If a precipitate is produced examine it according to (*page 82*) ..... **III.**

If, however, no precipitate forms in the above liquid add to it several drops of

Sodic Hydric Phosphate.

If a precipitate forms, see page 84 ..... **IV.**

If even after shakiny no precipitate appears, examine the fourth portion of the original solution according to (page 84) ..... **V.**

I. The Precipitate Obtained by Hydric Sulphide may be:

1. White. The precipitate is either separated sulphur and due, probably, to the presence of a ferric salt (comp. **IV.,** 7) or it may be zinc sulphide, due to too small an amount of free acid. Reject this precipitate and carry out exact examination for iron and zinc in the ammonic sulphide precipitate (see **II.,** page 82).

2. Yellow or Yellowish Red and will be CADMIC, STANNIC, ARSENOUS OR ANTIMONOUS SULPHIDE. Heat liquid with precipitate and allow it to stand until settled. Then pour off supernatant liquid as much as possible and warm (not boil) precipitate for a few minutes with 10-15 drops of yellow ammonic sulphide:

a. *Precipitate does not dissolve.* The original substance on being heated with sod. carb. before blowpipe on charcoal will give a rain-bow colored coating (comp. †**XXV.**) ..... **Cadmium.**

† "Reactions," Part I.

b. *Precipitate dissolves:* presence of tin, antimony and arsenic.

1a. Original solution gets turbid on addition of a large volume of water. Substance on being heated with sod. carb. before blowpipe on charcoal gives a white coating (comp. **IX.**) ..... **Antimony.**

2a. Precipitate some of original solution with hydric sulphide, and remove supernatant liquid. The precipitate is soluble in ammonic carbonate on warming. Original substance, heated before blowpipe on charcoal gives off a garlic-like smell (comp. **XII.**) ..... **Arsenic.**

3a. Hydric Sulphide will not produce a precipitate in original solution on previous addition of 3 vols. of conc. oxalic acid solution (comp. **X.**, *stannic salt*) ..... **Tin.**

3. Black or Brown and will be STANNOUS, LEAD, COPPER, BISMUTH, MERCURY OR SILVER SULPHIDE.

a. *Precipitate dissolves* on being heated with yellow ammonic sulphide, and hydrochloric acid throws down from this solution a yellow precipitate (comp. **X.**, *stannous salt*) ..... **Tin.**

b. Original solution with a large volume of water gives a white turbidity (comp. **VII.**) ..... **Bismuth.**

c. Original solution gives a white precipitate with dil. sulphuric acid (comp. **V.**) ..... **Lead.**

d. Hydrochloric acid causes a white precipitate in original solution which:

1a. Dissolves in ammonic hydrate (**XXI.**) ..... **Silver.**

2a. Is blackened by ammonic hydrate (**IX.**, *mercurous salt*) ..... **Mercury.**

e. Original solution (blue or green) is colored blue by ammonic hydrate (**I.**) ..... **Copper.**

f. Original solution yields a yellow precipitate on addition of sodic hydrate; a bright strip of copper turns white in the dil. orig. solution (**IX.**, *mercuric salt*) ..... **Mercury.**

II. The Precipitate Obtained by Ammonic Sulphide may be:

1. **Black** and will be IRON, NICKEL OR COBALT SULPHIDE.

a. *Precipitate dissolves readily in dil. hydrochloric acid;* the diluted solution yields a dark blue precipitate with potassic ferricyanide (IV., 6).....**Iron.**

b. *Precipitate did not dissolve;* but sodic carbonate gives with the original solution:

1a. A rose-red precipitate and orig. substance colors borax bead blue (XXVII.).....**Cobalt.**

2a. A light green precipitate (XXVI.)..... **Nickel.**

2. **Light Colored** and will be MANGANESE, OR ZINC SULPHIDE OR CHROMIC OR ALUMINIC HYDRATE.

a. Orig. substance fused with sod. carb. and nitre on platinum foil gives a green fusion (III.) .....**Manganese.**

b. Orig. substance fused with sod. carb. and nitre on platinum foil gives a yellow fusion (XXII.).....**Chromium.**

c. Orig. solution gives with sodic hydrate a white or grayish-white precipitate, dissolved by addition of an excess of sodic hydrate. From this solution will be thrown down by:

1a. †Hydric sulphide a white precipitate (II.).....**Zinc.**

2a. Nothing by hydric sulphide; but a white precipitate by ammonic chloride (XIII.).....**Aluminium.**

III. The Precipitate Obtained by Ammonic Carbonate may contain Barium, Strontium or Calcium.

The original solution will give:

†NOTE.—If the solution effected by sodic hydrate is not perfectly clear, filter before adding hydric sulphide or ammonic chloride; also warm after having added the same.

1. **A white precipitate** with CALCIC SULPHATE SOLUTION which:

a. *Appears at once.* Potassic dichromate, neutralized with ammonic hydrate, produces a yellow precipitate in orig. solution (VIII.) ..... **Barium.**

b. *Does not form until after some time.* Original solution gives no precipitate with potassic dichromate + ammonic hydrate. Original substance colors a flame red (XV.). **Strontium.**

2. **No Reaction** with CALCIC SULPHATE.

Original solution gives a white precipitate with ammonic oxalate (XIV.) ..... **Calcium.**

IV. If the Preceding "Chief Reagents" have not Affected the Original Solution, add some Ammonic Chloride, excess of Ammonic Hydrate and some Sodic Hydric Phosphate.

If a precipitate forms (perhaps *not without* aid of shaking), it shows the presence of (XIX.) ..... **Magnesium.**

V. Original Solution, having given no Reaction with preceding Reagents.

1. On being boiled with potassic hydrate, smells of ammonia (XVI.) ..... **Ammonium.**

2. Original substance on being introduced by platinum wire into the edge of a Bunsen flame, colors the same

a. Yellow (XX.) ..... **Sodium.**

b. Violet (XVII.) ..... **Potassium.**

B. Acids.

1. Pour some hydrochloric or nitric acid upon some of the original substance. If the fluid effervesces and the escaping gas is

a. *Colorless and odorless*, it is carbonic acid (**XIV.**). Substance is a.....**Carbonate.**

b. *Smelling like rotten eggs* and blackening paper soaked with lead acetate sol. (hydric sulphide, **XVIII.**), the substance is a.....**Sulphide.**

2. Acidulate the well diluted orig. solution with hydrochloric or nitric acid and add baric chloride. If *a white precipitate* is formed (**I.**, 9) the substance is a...**Sulphate.**

3. Moisten the loop of a platinum wire with conc. sulphuric acid, then dip into the substance under examination and introduce into the edge of the Bunsen flame (**XXIII.**), if the latter becomes green, the substance is a.....**Borate.**

4. Add ammonic chloride, an excess of ammonic hydrate and some magnesic sulphate to orig. solution. A white precipitate (often only after shaking) proves the substance to be a (**XX.**).....**Phosphate.**

5. †Original solution, acidulated with nitric acid, gives with argentic nitrate:

a. A white curdy precipitate, readily soluble in ammonic hydrate (**VIII.**, 8). Substance is a.....**Chloride.**

b. A yellowish precipitate, which does not dissolve on addition of ammonic hydrate. Original solution becomes blue on addition of some starch paste and a few drops of dil. fuming nitric acid (**XXIV.**). Substance is an.....**Iodide.**

6. If above tests do not determine the acid, pour some conc. sulphuric acid on a little of the original substance (no matter whether this produces a precipitate or not), add a copper turning, and heat.

†NOTE.—If solution contains a metal precipitated by ammonic hydrate, it must be removed by some appropriate process before adding argentic nitrate.

Or, add a little hydrochloric to a few drops of original solution and a few drops of sol. indigo, and heat. If red fumes of well known smell appear in the first, and if the liquid is discolored in the second case, the substance is a ..... **Nitrate.**

SECTION No. 2.

SIMPLE SUBSTANCES, SOLUBLE IN ACIDS ONLY.

A. Bases.

OUTLINE OF THE PROCESS.

If the substance is insoluble in water, heat a small knife-point full of it for a few minutes with some 10 or 15 drops of hydrochloric acid. When dissolved, heat to boiling and add some water. If any of the substance remains undissolved, pour off the above solution and repeat the operation with a fresh portion of hydrochloric acid. When everything is dissolved, heat to boiling before diluting the solution. If hydrochloric acid does not dissolve the substance try nitric acid.

The solution obtained is to be examined in the same manner as given above for "*Substances Soluble in Water.*" Attention needs only be called to a precipitate formed on diluting the original solution with water (indication of bismuth or antimony). *The above scheme* (*page 82*), *however, requires to be modified if the ammonic sulphide precipitate is light colored,* as it then need not necessarily contain one of the metals under **II.,** 2, but may contain one of the metals under **III.** and **IV.,** *provided the same be present as a phosphate or borate.* The phosphates or borates are re-precipi-

tated as light-colored substances from their solution in free acid as soon as the latter is neutralized by the addition of ammonic hydrate and ammonic sulphide.

In the case of simple substances insoluble in water, soluble in acids, portion **II.** *of the scheme* (SECTION 1) *will read as follows:*

II. The Precipitate obtained by Ammonic Sulphide may be:

1. **BLACK,** and will be SULPHIDE OF IRON, COBALT OR NICKEL; is to be examined as above (page 82).

2. **Light Colored or White;** PHOSPHORIC OR BORIC ACID MAY BE PRESENT. The precipitate will contain one of the metals MANGANESE, CHROMIUM, ALUMINIUM, ZINC, MAGNESIUM, CALCIUM, STRONTIUM BARIUM. Add dilute sulphuric acid and alcohol to original solution and shake.

A. *No precipitate is formed;* no calcium, strontium or barium present, but one of the following metals: Mn, Cr, Al, Zn, Mg.

a. Test with sod. carb. and nitre on platinum foil for (see page 82).....**Manganese.**

b. Test with sod. carb. and nitre on platinum foil for (see page 82).....**Chromium.**

c. Original solution gives a precipitate with sodic hydrate which, in excess of precipitant, is:

1a. Soluble; see page 82; test for..**Aluminium and Zinc.**

2a. Insoluble (a phosphate or borate of).....**Magnesium.**

B. *A precipitate is formed;* presence of either barium, strontium or calcium (as a phosphate or borate). In the original diluted solution dil. sulphuric acid will produce a precipitate

a. At once.....**Barium.**

b. Only after some shaking. The original substance moistened with hydrochloric acid imparts to a Bunsen flame the color of a salt of.....**Strontium.**

c. Not at all. The addition of alcohol to this liquid will produce a precipitate .....**Calcium.**

If ammonic sulphide produces no precipitate, barium, strontium, calcium, magnesium, cannot be present as a phosphate or borate. Consequently, the examination is continued according to **III.** and **IV.**, (Sec. 1.) as in page 82-84.

V. need not be considered, as all alkaline salts are soluble in water.

B. Acids.

In testing for acids, follow out in general the same scheme as above (page 84).

There are slight deviations only in the tests for phosphates, chlorides and iodides.

After having ascertained that the substance is neither a carbonate, sulphide, sulphate, borate nor nitrate (comp. page 86), proceed as follows:

To detect Phosphoric Acid, add to a few drops of original solution a drop or two of nitric acid conc. and 4 or 5 vols. of ammonic molybdate. A yellow precipitate, or at least a yellow coloration of the fluid after a *gentle* heating, indicates (comp. **XX.**, 3) a.....**Phosphate.**

The above method in the hands of beginners being liable to give erroneous results, additional evidence should be produced by way of precipitating with ammonic-magnesic phosphate. This test cannot be made in the usual way (page 86), as it requires a strongly ammoniacal solution. Ammonic hydrate, instead of decomposing the phosphate (with the formation of hydroxide of the base and ammonic phosphate),

simply re-precipitates the original substance from its solution in free acid, leaving behind a barren liquid, *i.e.*, the metal of the substance interferes with the ordinary way of testing, and must first be removed.

1. If the metal found is precipitated by hydric sulphide from acid solution, or if it is iron, nickel, cobalt, manganese or zinc, remove the metal by respectively hydric or ammonic sulphide and filter off the metallic sulphide. The filtrate contains ammonic phosphate, and may be tested according to page 86 for a ..... **Phosphate.**

2. If the metal found is aluminium or chromium, ammonic sulphide would throw down the phosphate. No such precipitate will form if tartaric acid and then excess of amm. hydrate is added to orig. solution. Test this clear solution according to page 86 for a..... **Phosphate.**

3. If the metal found is barium, strontium or calcium, remove it by dil. sulphuric acid and alcohol. Test the filtrate with excess of amm. hydr. and magnesic sulphate for a.. **Phosphate.**

4. If the metal is magnesium, moisten some of the original *substance* with a com. sol. of argentic nitrate. A yellow coloration produced indicates a..... **Phosphate.**

To detect a **Chloride or Iodide,** it is necessary to dissolve the substance in nitric acid. Argentic nitrate then will produce a curdy precipitate which, after filtering and washing, is to be washed through the perforated filter into a test tube, placed under the funnel.

a. Precipitate dissolves in ammonic hydrate on gentle warming. Substance is a..... **Chloride.**

b. Precipitate does not dissolve. Substance is an.. **Iodide.**

In dissolving a substance in hydrochloric acid observe whether chlorine is liberated on boiling. In this case the substance is either a peroxide or chromate (comp. **VI., XVIII., XXII.**)

SECTION No. 3.

SIMPLE SUBSTANCES, INSOLUBLE (OR NEARLY SO) IN BOTH WATER AND ACIDS.

The sulphates of calcium, strontium, barium and lead, chloride and iodide of silver, ignited chromic acid, and also charcoal and sulphur belong to this class; the latter two may be easily recognized from their color and their behavior before the blowpipe.

Pour some ammonic sulphide on the substance:

1. *It remains unchanged;* no lead or silver compound.

a. Original substance is green, and gives a yellow fused mass with sod. carb. and nitre before blowpipe on platinum foil. ..... **Chromic Oxide.**

b. Original substance is white. Boil a small knife-point full of the *fine* powder with a conc. sol. of sodic carbonate for about 10 minutes; pour off the supernatant liquid and boil once again with more of the sodic carbonate solution; filter, wash the residue on the filter well and dissolve it, by pouring on dil. hydrochloric acid. Test this filtrate for barium, strontium, calcium (page 84); the sodic carb. sol. poured off the first time, to be tested for sulphuric acid (page 86).

2. *Ammonic sulphide turns the substance black*; fuse the substance with sod. carb. on charcoal before the blowpipe. The result is:

a. A malleable metallic globule and a fusion which blackens moist silver. Substance is..... **Plumbic Sulphate.**

b. A metallic globule and a fusion which does not blacken moist silver. In this case fuse some of the substance with sod. carb. on porcelain cover, dissolve the fusion in water and filter. Dissolve the well washed residue in nitric acid and test with hydrochloric acid for SILVER. Acidulate filtrate obtained above with nitric acid and test one part with argentic nitrate for CHLORINE, the other one with starch paste and dil. fuming nitric acid for IODINE (page 86).

CHAPTER II.

EXAMINATION OF COMPLEX SUBSTANCES SOLUBLE IN WATER OR IN ACIDS.

It is to be understood that of the elements treated on hitherto, chromium and strontium are excluded, and that of the metals tin, antimony and arsenic, only one at a time shall be present; as also of the metals nickel and cobalt.

A. Bases.

OUTLINE OF THE PROCESS.

Heat a small knife-point full of the substance in a test tube one-third full of water. If it dissolves completely add some 6-10 drops of hydrochloric or nitric acid. If the substance is wholly or partly insoluble heat a small knife-point full with hydrochloric or nitric acid in the manner indicated on page 84. (Sec. 2.)

To one-third of this solution add a little

Hydric Sulphide.

If a precipitate is formed add hydric sulphide *until the solution* AFTER SHAKING *smells of it distinctly*, warm and filter. The precipitate may contain TIN, ARSENIC, ANTIMONY, MERCURY, LEAD, SILVER, COPPER, BISMUTH, and CADMIUM. The filtrate may contain the other heavy metals, metals of the earths, alkaline earths and alkalies.

Wash the precipitate on the filter by pouring upon it repeatedly hot water and examine it according to.....**I.**

Add a little more hydric sulphide to the filtrate in order

to ascertain whether or not everything precipitable has been removed; then add some ammonic chloride, supersaturate with ammonic hydrate and, no matter whether this produces a precipitate or not, add

Ammonic Sulphide,

Drop by drop as long as a reaction can be observed. If hydric sulphide failed to produce a precipitate, reject the (thus diluted) liquid and add to a second third of the original solution an excess of ammonic hydrate and then ammonic sulphide.

The precipitate obtained in either way may contain NICKEL, COBALT, IRON, MANGANESE, ZINC and ALUMINIUM, and if PHOSPHORIC or BORIC acid are present, also MAGNESIUM, CALCIUM and BARIUM. Warm this precipitate with the liquid, filter, wash *well* and examine the precipitate according to ..... **II.**

To the filtrate from the ammonic-sulphide precipitate, or if no such precipitate was formed, to the original liquid add

Ammonic Carbonate.

A precipitate obtained will contain CALCIUM and BARIUM. Filter off and examine precipitate according to . **III.**

Examine the filtrate from this precipitate, or if none was formed, the clear liquid itself with ammonic hydrate and:

Sodic Hydric Phosphate.

A precipitate indicates **Magnesium**; see ..... **IV.**
Examination for **Alkali Metals** according to.... **V.** and **VI.**

I. The precipitate obtained by Hydric Sulphide may be:

1. **White** from separated sulphur, which is an indication of a ferric salt (comp. page 14).

2. Yellow, Brown or Black. Filter off precipitate and wash it *well;* perforate the bottom of the filter with a match or a glass rod, and rinse the precipitate into a test tube (placed under the funnel) by the aid of a jet of water from the wash bottle. †Allow precipitate to settle, pour off the supernatant water, and *warm* precipitate with *yellow* ammonic sulphide. This will dissolve the precipitate either wholly or partially or not at all.

If the precipitate dissolves perfectly, only one of the metals, *tin*, *antimony* or arsenic, can be present and the examination is conducted according to ..... **A.**

If the precipitate does not dissolve, or only partially, filter off the undissolved portion and

Examine filtrate, according to ..... **A.**

Examine residue, according to ..... **B.**

A. Tin, Antimony or Arsenic.

Dilute the filtrate or the ammonic sulphide solution well with water and acidulate with hydrochloric acid. The precipitate obtained is:

a. *White* from separated sulphur, merely the result of decomposition of ammonic sulphide.

b. *Yellow* or reddish, and may contain *tin*, *antimony* or *arsenic*. Filter off precipitate, wash well, and rinse one-half of it from perforated filter into a test tube. Allow precipitate to settle, pour off supernatant water as much as possible, and dissolve precipitate by boiling with a very *small* quantity of aqua regia. Divide solution into three parts. *To one part add* 3 vols. of conc. oxalic acid and hydric sulphide.

†NOTE.—Sometimes the hydric sulphide precipitate, after having been rinsed from perforated filter, will settle very slowly. Addition of a few drops of hydrochloric acid and gentle heating will shorten very much the time required for settling.

1a. Nothing is precipitated.....**Tin.**

2a. A precipitate forms again: The metal is *arsenic* or *antimony.* Add hydric sulphide to a *second part of the aqua regia solution.* The precipitate formed redissolves on warming with ammonic carbonate. Test some of the precipitate left on perforated filter before the blowpipe on charcoal. A garlic-like smell is given off.....**Arsenic.**

3a. The third portion of the aqua regia solution becomes turbid on the addition of a large quantity of water. The precipitate on perforated filter gives a strong white coating on charcoal before the blowpipe.....**Antimony.**

B. Mercury, Lead, Silver, Copper, Bismuth and Cadmium.

The sulphides of these metals constitute that portion of *the hydric sulphide precipitate which is insoluble in ammonic sulphide.* Wash this residue well and rinse it from perforated filter into a test tube; allow to settle, pour off the supernatant water and boil with *a little* conc. nitric acid. The sulphides will either dissolve completely (leaving only a dirty yellow mass of sulphur floating in the nitrate solution), or a black or gray powder will remain, which sinks to the bottom rapidly.

a. Filter off this *insoluble residue;* wash, rinse from perforated filter, etc., and dissolve in the least possible amount of aqua regia. Immerse a copper turning into this solution, after previous dilution with some water. The copper will turn white from .....**Mercury.**

b. *The filtrate* (a) from the separated sulphur or black insoluble residue, may give a white precipitate with dil. sulphuric acid and a little alcohol.....**Lead.**

c. The filtrate from **b**, or, if sulphuric acid and alcohol did not precipitate anything, the liquid itself gives a white curdy precipitate with hydrochloric acid.....**Silver.**

d. Supersaturate the filtrate from **c**, or, if hydrochloric acid produced no precipitate, the liquid itself with the least possible amount of ammonic hydrate. The result is:

1a. A blue solution ..... **Copper.**

2a. (With or without blue solution) a white precipitate. Filter and wash the same and dissolve it on the filter with a few drops of hot hydrochloric acid. This solution will give a white precipitate when largely diluted with water..... **Bismuth.**

e. †The ammoniacal solution (**d** 1a) may contain cadmium as well as copper. In this case the addition of sodic hydrate, with heating, will produce a white precipitate, which after filtering and washing is dissolved by hydrochloric acid. Hydric sulphide precipitates from this solution yellow cadmic sulphide..... ..... **Cadmium.**

II. ‡*The Ammonic Sulphide precipitate* is filtered off and washed well, keeping it covered with hot water all the time. Dissolve precipitate on the filter with the *least possible* amount of hot dil. hydrochloric acid (1 vol. acid+ 4 vols. water). Pour the filtrate back on the filter repeatedly, after having heated it each time to boiling. This will

†NOTE.—If solution **d** contains a large amount of free acids, the ammoniacal copper-cadmium sol. may be surcharged with ammonic salts to such an extent as to prevent sodic hydrate from producing any precipitate. In this case precipitate the cadmium (with or without copper) by hydric sulphide, and test precipitate before blowpipe on charcoal for cadmium. If no copper is present cadmium may be detected by hydric sulphide in the ammoniacal filtrate from the bismuth precipitate.

‡NOTE.—If the substance under examination contains a large amount of metals of the hydric sulphide group, the filtrate from their sulphides will be a very dilute solution of the following metals. It should be concentrated in a porcelain dish before addition of ammonic hydrate and ammonic sulphide.

give a clear filtrate, free from hydric sulphide (which if not removed would eventually interfere with the following tests):

1. **†If a black residue is left on the filter** either cobalt or nickel is present; after washing out, test as follows:

a. A small quantity of it colors the borax bead blue. **Cobalt.**

b. Rinse precipitate from perforated filter, etc., and dissolve in the least possible amount of nitric acid. Sodic carbonate produces a light green precipitate in this solution..... **Nickel.**

2. **The Filtered HCl Solution of the Ammonic Sulphide Precipitate,** if the latter was black, must be boiled with several drops of nitric acid in order to convert any iron that may be present into a ferric salt. Hence, omit the addition of nitric acid if precipitate was not black. This solution *may contain iron, manganese, aluminium and zinc,* and, if substance contains phosphoric or boric acid, also *barium, calcium and magnesium.* The method of examination being comparatively complicated and tedious in the latter case, but simple in the absence of phosphoric (and boric) acid, their presence or absence and the course to pursue should be determined at this moment. To detect phosphoric acid in solution 2, dilute a few drops of it with water, add a drop or two of nitric acid and 10-15 drops of ammonic molybdate and warm (comp. **XX.,** 3). (‡Test for boric acid according to page 116.)

†NOTE.—The only safe method to determine both cobalt and nickel in one substance is as follows: Dissolve the black precipitate in nitric acid, slightly supersaturate the liquid with potassic hydrate, add a sol. of potassic-nitrite and acidulate with acetic acid. Filter off the precipitate of potassic-cobaltic nitrite, which will form after a time and throw down the nickel in filtrate with sodic carbonate.

‡NOTE.—The original in this paragraph, does not mention boric acid, apparently assuming that, as a rule, the salts are

A. If no Phosphoric (or Boric) Acid is present, add an excess of sodic hydrate: a permanent precipitate *may contain manganese and iron,* the alkaline liquid *aluminium and zinc.*

a. Filter off and wash the precipitate; ignite a little of it with sodic carbonate and nitre on platinum foil. The fused mass is green.....**Manganese.**

b. Dissolve the greater part in a *small* amount of hydrochloric acid. Potassic ferrocyanide gives in this solution a dark blue precipitate.....**Iron.**

c. †To part of the alkaline filtrate add ammonic chloride. A precipitate indicates .....**Aluminium.**

d. Add some hydric sulphide to the balance. A precipitate shows .....**Zinc.**

B. If Phosphoric (or Boric) Acid have been found, the *solution may contain barium, calcium and magnesium* besides the metals given under **A.** First, barium and calcium are removed as sulphates.

a. Add to solution 2 (page 108) dilute sulphuric acid. Precipitate indicates .....**Barium.**

b. Filter off such precipitate and add an equal vol. of alcohol to the filtrate. Precipitate (perhaps only on shaking) .....**Calcium.**

c. Reject wash water from **b**; heat (not boil) the filtrate

so selected that the ammonic sulphide precipitate does not contain boric acid: to always conduct examination according to B. might confuse beginners and a previous accurate test for Boron be too difficult for them.

†NOTE.—If the sodic hydrate solution was not quite clear, filter the alkaline aluminium-zinc solution before adding hydric sulphide or ammonic chloride. Warming the liquid moderately for a time, after the addition of these reagents causes the transparent precipitates to shrink together and come out plainer to view.

from **b** for quite a time with excess of sodic hydrate and filter off any permanent precipitate: *ferric*, *manganous*, and *magnesic hydrates* (**d**).

1a. The alkaline filtrate, containing the **Aluminium and Zinc** (as well as the phosphoric and boric acid of the solution) is to be tested for the two metals as above under **A.**

D. The precipitate (**D**) may contain iron, manganese and magnesium.

1a. †Test a small portion of it, by fusing with sod. carb. and nitre, green fusion ..... **Manganese.**

2a. The greater portion of the precipitate should be washed well and then dissolved on the filter with a little dil. hydrochloric acid. Divide this solution into two parts:

Test one part with potassic ferrocyanide. A blue precipitate indicates ..... **Iron.**

3a. From the balance of solution precipitate iron and manganese with ammonic hydrate and sulphide; filter off and precipitate from filtrate with sodic hydric phosphate.... **Magnesium.**

Unless the barium, calcium and magnesium were carried into the ammonic sulphide precipitate by phosphoric (or boric) acid, they will be found in the remaining two subdivisions.

III. The Ammonic Carbonate precipitate may contain barium and calcium. Wash it on the filter and dissolve by addition warm dil. hydrochloric acid. Add dil. sulphuric acid to the solution:

a. A precipitate forms at once..... **Barium.**

†NOTE.—Chromium, in absence of manganese, may be found best in salt mixtures by fusing some of the ammonic sulphide precipitate with sod. carb. and nitre on platinum foil. If chromium is present, the fusion is yellow and the solution in water is of the same color.

b. Filter off that precipitate and add to the filtrate ammonic hydrate and oxalic acid. A precipitate indicates..... **Calcium.**

IV. †The precipitate obtained by Sodic Hydric Phosphate indicates ..... **Magnesium.**

V. To test for Ammonium, boil the original substance with sodic hydrate. Any ammonia escaping is easily recognized by its smell and its turning moist red litmus paper blue ..... **Ammonium.**

VI. ‡To test for Potassium and Sodium, remove in a portion of original solution all constituents precipitable by hydric sulphide, ammonic sulphide and ammonic carbonate; evaporate filtrate to dryness in a porcelain dish, and heat residue until all ammonic salts are volatilized. A residue obtained:

a. Colors a Bunsen and spirit lamp flame yellow.. **Sodium.**
b. Colors a flame violet..... **Potassium.**

B. Acids.

The examination of above substances for acids is conducted in the same manner as given in the analysis of "*simple substances*" (comp. pages 84 and 92). *Special attention must be paid to the rules laid down on page 68.*

†NOTE.—Before precipitating magnesium, convince yourself with oxalic acid that barium and calcium have been thrown down completely.

‡NOTE.—If potassium and sodium are present at the same time, the yellow sodium flame will completely hide the violet potassium color. The latter may be detected through a blue glass (cobalt glass). Potassium may also be detected as potassic bitartrate: Dissolve the residue from evaporation in a few drops of warm water and filter. Add to filtrate a drop or two of sodic carbonate and then tartaric acid sol. A precipitate (perhaps only upon shaking) indicates.. **Potassium.**

1. **Carbonates** and **Sulphides** are recognized upon heating with hydrochloric acid (page 84) odor or effervescence.

2. Heating the substance with conc. sulphuric acid and a copper turning (brown fumes), or with hydrochloric acid and sol. indigo (fading of color), indicates the presence of a. **Nitrate.**

3. †Add baric chloride to the highly diluted solution which has been acidulated with hydrochloric acid. A white precipitate shows the presence of a..... **Sulphate.**

4. To detect boric acid, remove with hydric sulphide and with sulphuric acid and alcohol all these constituents which color the flame (copper, barium and calcium) and evaporate the filtrate to dryness. Moisten the residue with conc. sulphuric acid and introduce the pasty mass on platinum wire into the edge of a flame. A green color indicates a..... **Borate.**

5. To prove the presence of chlorides and iodides dissolve the substance in nitric acid, add argentic nitrate to the diluted solution and filter off. Rinse the well-washed precipitate from the filter and warm slightly with ammonic hydrate. The precipitate dissolves:

a. Completely; presence of only a..... **Chloride.**

b. Imperfectly. Filter off the residue, and acidulate filtrate with nitric acid. A precipitate indicates a..... **Chloride.**

6. To prove the presence of iodine, add to the well diluted original solution a little starch paste and a drop or two of dil. nitric acid fuming (comp. **XXIV.**, 4, page 66). A blue color proves the presence of an..... **Iodide.**

7. To a drop of original solution, diluted with a little water, add a few drops of nitric acid and excess of ammonic molybdate. A yellow precipitate (or at least coloration) shows the presence of a..... **Phosphate.**

Or: Remove with hydric sulphide, sulphuric acid and alcohol

†NOTE.—If hydrochloric acid produces a precipitate, filter off before adding baric chloride.

all the elements precipitable in this way. Concentrate the filtrate if necessary, and heat with excess of conc. sodic hydrate and filter off precipitate. The phosphoric acid is concentrated in this alkaline liquid (comp. pages 92, 94). As it also contains the aluminium of the substance it is necessary to acidulate the liquid with tartaric acid before it may be tested with ammonic hydrate and magnesic sulphate for a ..... **Phosphate.**

C. Alloys.

In analyzing alloys it is useless, of course, to test for acids as well as in the majority of cases for the metals of the alkalies and alkaline earths, as they very rarely occur in alloys.

Use conc. nitric acid to dissolve alloys, warming a few pieces (as small as possible) of the alloy until the metal has disappeared.

If there is a white residue, it is either stannic or antimonous acid, which should be filtered off, washed well and dissolved by boiling with hydrochloric acid. Examine the solution obtained according to page 102.

The solution of the alloy in nitric acid contains all other metals; dilute somewhat with water and precipitate the *silver*, that may be present, by addition of a few drops of hydrochloric acid. Filter off the curdy precipitate and throw down the *lead* present as sulphate by the addition of dil. sulphuric acid and some alcohol. The filtrate of this precipitate is examined with hydric and ammonic sulphide in the ordinary manner described above (page 98).